



YoungRad-seminar Proceedings Helsinki 14-15 December 2006

Strålberg, Elisabeth; Petersen, Roongrat; Salminen, Susanna; Sidhu, Rajdeep

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Nordisk kjernesikkerhetsforskning
Nordisk kärnsäkerhetsforskning
Nordic nuclear safety research

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YoungRad-seminar Proceedings Helsinki 14-15 December 2006

Elisabeth Strålberg (ed.)¹, Roongrat Petersen²
Susanna Salminen³ and Rajdeep Sidhu¹

¹ Institute for Energy Technology, Norway

² Technological University of Denmark, Denmark

³ University of Helsinki, Finland

September 2007

Abstract

To provide an inspiring working environment for young students and scientists, it is important that they at an early stage can take part in a network of scientists working in their fields of interest. However, within each of the five Nordic countries the network of people involved in the fields of radiophysics, radiochemistry, radioecology, radiation protection and other related fields is rather small. Educational networking is a key factor in keeping young researchers motivated to continue working within these fields, and to recruit new students.

For that reason the first YoungRad-seminar was held in Helsinki 14-15 December 2006. 43 young participants including MSc and PhD students at universities, researchers at different institutes and personnel from Nordic authorities took part in the seminar. All Nordic countries except Iceland were represented. The seminar was divided into four sessions including oral and poster presentations. In addition two senior researchers were invited to speak about Nordic radioecology and NKS. This report contains the abstracts and presentations made at the seminar.

Key words

Seminar, young scientists, radiophysics, radiochemistry, radioecology, radiation protection

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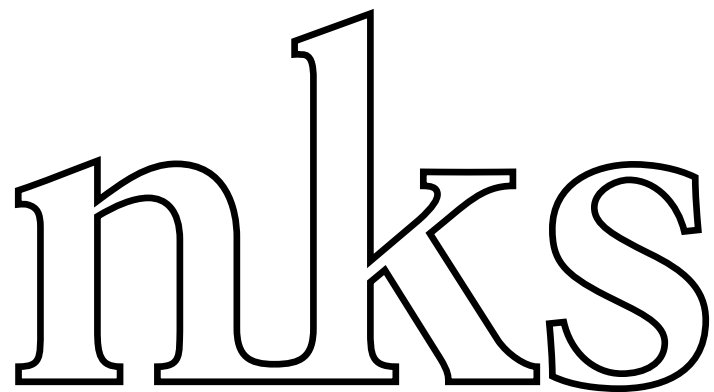
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NKS Secretariat
NKS-776
P.O. Box 49
DK - 4000 Roskilde, Denmark

Phone +45 4677 4045
Fax +45 4677 4046
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YoungRad-seminar Proceedings

Seminar for young scientists in the fields of
radiophysics, radiochemistry, radioecology,
radiation protection and related fields

Helsinki 14-15 December 2006



Elisabeth Strålberg (ed.), Roongrat Petersen, Susanna Salminen and Rajdeep Sidhu

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Introduction

To provide an inspiring working environment for young students and scientists, it is important that they at an early stage can take part in a network of scientists working in their fields of interest. However, within each of the five Nordic countries the network of people involved in the fields of radiophysics, radiochemistry, radioecology, radiation protection and other related fields is rather small. Educational networking is a key factor in keeping young researchers motivated to continue working within these fields, and to recruit new students.

During the last two decades there has been a dramatic decrease of new students in these disciplines. As IAEA states “The nuclear workforce is aging - that is, more and more nuclear workers are approaching retirement age, without a corresponding influx of appropriately qualified younger personnel to replace them. Fewer young people are studying nuclear science, nuclear engineering and related fields at the university level, and a growing number of universities are giving up their nuclear education programmes altogether”. IAEA has taken this concern about decline in nuclear expertise seriously and have started a programme called “Nuclear Knowledge Management” (<http://www.iaea.org/km/>) to preserve past, present and future knowledge.

As stated by M. Rossbach (IAEA) at the conference on “Low Level Radioactivity Measurement Techniques” in Vienna in October 2003; “In many countries, particularly in Europe and the United States, a gradual decrease of teaching and training opportunities in nuclear and radiochemistry has been observed since more than two decades”. Similar trends are seen in the Nordic countries, and the situation was also discussed at the last NSFS meeting in Rättvik, Sweden.

Most students at universities do not know about fields they can work within and places they can work at after education. We believe that a congress like this provides stronger communication between different institutes and universities. We strongly believe that close collaboration between young researchers and also between generations in the Nordic community will ensure exchange of experience and a dynamic development in the fields. Obtaining and maintaining contact with scientists in the other Nordic countries will also encourage and stimulate cooperation between the different institutes and universities, and are therefore of greatest importance.

The YoungRad-seminar was held in Helsinki 14-15 December 2006. 43 young participants including MSc and PhD students at universities, researchers at different institutes and personnel from Nordic authorities took part in the seminar. All Nordic countries except Iceland were represented. A guided tour at the radiochemistry laboratories at Helsinki University and Finnish Meteorological Institute was arranged prior to the seminar. The seminar was divided into four sessions including oral and poster presentations. In addition two senior researchers were invited to speak about Nordic radioecology and NKS. This report contains the abstracts and presentations made at the seminar.

Agenda

Wednesday 13 December

14:30 – 17:30 Guided tour at the laboratories at Helsinki University and Finnish Meteorological Institute (voluntarily)

Thursday 14 December

09:00 – 10:00 Registration

10:00 – 10:10 Opening of YoungRad Seminar

10:10 – 11:30 Session I: Nuclear fuel and waste

Chairman: Elisabeth Strålberg

10:10 – 10:30 Andreas Knutsson, Chalmers University of Technology, Sweden
Radionuclide sorption onto biofilm covered apatite and quartz minerals

10:30 – 10:50 Åsa Magnusson, Lund University, Sweden
Waste arising and local environmental effects caused by ^{14}C production in various types of nuclear reactors

10:50 – 11:10 Joachim Holm, Chalmers University of Technology, Sweden
Chemistry under severe accidents

11:10 – 11:30 Kristin Fure, Institute for Energy Technology, Norway
An automated system for performing two dimensional gamma spectroscopy measurements of fuel rod

11:30 – 12:20 Coffee break and posters (session I):

Anumaija Leskinen, University of Helsinki, Finland
Determination of granites mineral specific porosities by PMMA method and FESEM/EDAX

Jarkko Kyllönen, University of Helsinki, Finland
Sorption of Cs to biotite

Laura Togneri, University of Helsinki, Finland
Radioactivity distribution analysis with digital autoradiography at HYRL

Maarit Kelokaski, University of Helsinki, Finland
Visualisation of conductive pore space by ^{14}C -PMMA impregnation

12:20 – 13:00 Session I continuing

12:20 – 12:40 Risto Koivula, University of Helsinki, Finland
Selective sorption properties of inorganic materials

12:40 – 13:00 Teemu Kärkelä, VTT, Finland
Transport of ruthenium in diverse oxidising conditions

13:00 – 14:00 Lunch

14:00 – 15:00 Session II: Radiopharmacy and dosimetry

Chairman: Susanna Salminen

- 14:00 – 14:20 Anna Kirjavainen, University of Turku, Finland
[¹⁸F]fluoromethane as a precursor for ¹⁸F-labelling synthesis of radiopharmaceuticals for Positron Emission Tomographic (PET) imaging studies
- 14:20 – 14:40 Heli Mononen, STUK, Finland
Non-targeted effects of ionising radiation - bystander effect and genomic instability
- 14:40 – 15:00 Håkan Gustafsson, Linköping University, Sweden
EPR dosimetry using lithium formate for measurements in narrow radiation fields

15:00 – 15:30 Coffee break and posters (session II):

- Risto Paintner, MAP Medical Technologies Oy, Finland
A case study of radiopharmaceutical production (¹⁸F]FDG) at the University of Helsinki
- Tiina Lipponen, University of Helsinki, Finland
¹⁸F-Radiochemistry in the University of Helsinki

15:30 – 16:30 Session II continuing

- 15:30 – 15:50 Johanna Rokka, Turku PET Centre, University of Turku, Finland
[¹⁸F]FDG and its radioactive metabolites in biological samples
- 15:50 – 16:10 Semi Helin, Turku PET Centre, University of Turku, Finland
Production of high specific radioactivity radiopharmaceuticals from [¹¹C]methane
- 16:10 – 16:30 Stewart Makkonen-Craig, University of Helsinki, Finland
Recent applications of Helsinki's cyclotron

19:00 Refreshments and conference dinner

Friday 15 December

09:00 - 09:30 Invited Speaker – Elis Holm, University of Lund, Sweden

Five decades of Nordic Radioecology

09:30 – 10:30 Session III: Environmental radioactivity and applications

Chairman : Roongrat Petersen

09:30 – 09:50 Elisabeth Strålberg, Institute for Energy Technology, Norway

Activities at the Environmental Monitoring Section at Institute for Energy Technology (IFE), Norway

09:50 – 10:10 Mohamad Zakaria, Malmö Högskola, Sweden

“Atoms for peace”? Nuclear Energy and Sustainable Peace

10:10 – 10:30 Ole-Christian Lind, Norwegian University of Life Sciences, Norway

Radioactive particles originating from events involving nuclear weapons

10:30 – 11:00 Coffee break and posters (session III):

Jarkko Ylipietä, STUK, Finland

Time series and correlations in ^{137}Cs concentrations in the fish fauna of the lake Apukkajärvi in Finnish Lapland

Kaisa Vaaramaa, University of Helsinki, Finland

Soluble and particle bound ^{238}U -series radionuclides in ground waters

Miia H. Palosaari, University of Helsinki, Finland

Detection of irradiated foods by the thermoluminescence of mineral contamination

11:00 – 11:40 Session III continuing

11:00 – 11:20 Sven K. Hartvig, Institute for Energy Technology, Norway

Radioactive tracers for oil reservoirs - concept, tracers and analysis

11:20 – 11:40 Roongrat Petersen, Technical University of Denmark, Denmark

Evaluation of degree of readsorption of radionuclides during sequential extraction in soil: comparison between batch and dynamic extraction systems

11:40 – 12:40 Lunch

12:40 – 14:00 Session IV: Radiochemistry and analytical techniques

Chairman : Rajdeep Sidhu

12:40 – 13:00 Lindis Skipperud, Norwegian University of Life Sciences, Norway

Measuring Pu isotope ratios with mass spectrometry¹

13:00 – 13:20 Natallia Torapava, Swedish University of Agricultural Sciences, Sweden

EXAFS technique for structure determination of metal ions in the solution

13:20 – 13:40 Susanna Salminen, University of Helsinki, Finland

Study of changes in U oxidation states during anoxic sample dissolution

13:40 – 14:00 Rajdeep Sidhu, Institute for Energy Technology, Norway

Radiochemistry at the Environmental Monitoring Section at Institute for Energy Technology (IFE), Kjeller, Norway

14:00 – 14:30 Coffee break and posters (session IV):

Jussi Jernström, University of Helsinki, Finland

Novel chromatographic separation methods for Pu and Am

14:30 – 15:00 Invited speaker – Sigurður Emil Pálsson, NKS-B Programme

Manager NKS: Supporting five decades of Nordic Radioecology – What now?

15:00 – 15:30 Concluding remarks and discussion

15:30 End of seminar

¹ Lindis Skipperud was unfortunately not able to participate in the YoungRad seminar. Her presentation is therefore not included in this report.

INVITED SPEAKERS

Elis Holm

Five Decades of Nordic Radioecology

Sigurður Emil Pálsson

*NKS: Supporting Five Decades of Nordic Radioecology.
What now?*

Five Decades of Nordic Radioecology

Elis Holm

Department of Medical Radiation Physics, Lund University, Sweden /
Centro Nacional de Aceleradores, Seville, Spain

Abstract

Our present form of radioecology is multidisciplinary and a better wording is perhaps Environmental Radioactivity Research. The Nordic Countries were for some decades among the leading countries in this research. A series of events during the last 4-5 decays has made it possible to continue the work such as.

- during the 60ies nuclear tests and their effects.
- during the 70ies the construction of nuclear power plants.
- during the 80ies the impact of European reprocessing plants in temperate and Arctic waters of the North Atlantic.
- during the 90ies NORM, TENORM studies, studies of long-lived radionuclides and chemico-physico form of radionuclides.
- in the new millennium to maintain and build up competence of new scientists in the field of Environmental radioactivity, hot particle studies and emergency preparedness.

The 1950ies

In principle the release of radioactive elements were known from the first nuclear tests. It is however often a miss belief that the major damage comes from the radioactivity. It is the heat and shock waves which are much more important.

In principle radioecology started in 1957, i.e. 49 years ago when the Windscale accident happened. There was a significant release of ^{131}I . As we all know it is raining a lot in Bergen, Norway and there was a concern if people had an internal contamination of ^{131}I in the thyroid.

In Lund, Sweden there was one of the first whole body counters set up for controlling if people working at the Nuclear Medicine department were contaminated.

A couple of Norwegians from Bergen were sent to Lund for whole body measurement. As expected they found ^{131}I but to their surprise also ^{137}Cs . There was no reporting of releases of ^{137}Cs from the Windscale facility. At the same time the first large nuclear tests had been conducted but according to military people and politicians the radioactivity released from the tests would be diluted the atmosphere, completely harmless and it should not be possible to detect anything in man from such tests. Up to 1958 more than 250 test explosions had taken place and fission materials equivalent to 92 MT TNT had been released.

The 1960ies

In the beginning very much was focused on the consumption of goat cheese as the major intake of radiocaesium. *“Preliminary measurements made at the Radiation Physics Department in Lund of the caesium-137 content in five Norwegians indicated that Norwegian inhabitants could have higher body-burdens than those reported for people elsewhere (Nature, 1961). Another group of Norwegians (from Bergen and*

Oslo) were later sent to Lund and the results were correlated to the daily consumption of goat cheese and milk.

The scientists, Liden, Baarli, Madshus and Mc Call therefore, in order to ensure this fact, sent two people from Kautokeino in northern Norway to Lund for whole body counting. They found no traces of ^{131}I in their bodies but to their surprise significant amounts of ^{137}Cs . This proved that it was reindeer meat which was the cause of the high body burdens of ^{137}Cs (Fig. 1).



Fig. 1. Picture stolen from some Norwegian document.

This knowledge started a very intensive research in the Nordic countries and also Russia and Canada. Other radionuclides (fission products) but also natural radionuclides such as ^{210}Po and ^{210}Pb were found to be enhanced the body by consumption of reindeer meat. Radiochemical separations and alpha spectrometry was developed especially when the Silicon detector (surface barrier) became available. The development of semi conductor detectors made it possible to study rather complex spectra. Development of radiochemistry made it possible to analyse elements such as ^{55}Fe (IC 100%) and ^{90}Sr (100% β) by gas flow counting. Actually the most sensitive method to analyse ^{137}Cs and ^{60}Co still is radiochemical separation and beta counting.

In 1968 the loss of nuclear weapons at Thule, Greenland initiated the study of plutonium in the environment at Risoe Nat Lab. (There had been a previous similar accident in 1966 at Palomares, Spain). The following was stated by Lidén, 1962: ”Att den radioaktiva nedskräpningen av vår jord inte får tillåtas fortsätta i samma takt som hitintills, är något som jordens alla folk genom saklig upplysning måste övertygas om. Det begränsade utrymmet för ett strålningstillskott utöver den naturliga strålningen, ett tillskott, som vi är beredda att acceptera, måste reserveras

för medicinska och tekniska användningar av joniserande strålning i avsikt att förbättra vår hälsa och våra levnadsvillkor”.

In 1966 many countries signed an agreement to not conduct atmospheric nuclear tests.

The 1970ies

During this period several publications and academic dissertations on environmental radioactivity were produced. For some reason there was no intensive collaboration between the physicists/radiochemists and “real” ecology departments.

Other environments such as the sea and lakes became of interest. The nuclear power plants were built in Sweden and Finland and activation products were found in the vicinity of them especially by using *Fucus sp.* as bioindicators. Radiocaesium and plutonium was also found. Plutonium levels at the Swedish west coast decreased with time while radiocaesium did not, which we at that time could not explain. In Norway the monitoring of the sea had ceased since levels earlier had been shown to decrease.

The Laboratory of Marine Radioactivity was established in Monaco, 1962, in order to investigate the possibility to use the sea for nuclear waste disposal. In 1972 the so-called London Convention was adopted and seabed disposal was no longer allowed. The laboratory later changed to Marine Environment Laboratory.

The 1980ies

It was not until the early 80ies we understood the importance of the European reprocessing facilities and that radioactivity was transported by currents to Sweden and Norway. The Windscale/Sellafield/Seascale facility had been in operation since 1952, but large releases did not occur until around 1978. During the YMER-80 expedition ¹³⁷Cs levels in surface seawater were up to 100 Bq/l, decreasing from South to North of Norway. When this was published the director plus another person came to Lund and told me that this was impossible. The releases from Sellafield must be harmless and be diluted in the whole north Atlantic. The measurements must be wrong or there was some run-off from Norwegian rivers. They would never start any significant radioecological research again in Norway. They had of course not foreseen the Chernobyl accident a few years later.

Analysis of ⁹⁹Tc in the environment started and again brown algae were shown to be excellent bioindicators. Since ⁹⁹Tc was found around Barseback nuclear power plant we suspected that this was the origin even if it was mainly a fission product. A survey along the coast showed that the concentrations increased with distance northwards. Again it was obvious that the activity originated mainly from the Sellafield reprocessing plant.

Intensive expeditions were undertaken in the Baltic Sea, and temperate waters of the North Atlantic and even the Antarctic. The use of the released radioactivity for mapping and modelling water transport in time and space was very successful. The Chernobyl accident intensified Nordic collaboration not at least through NKS.

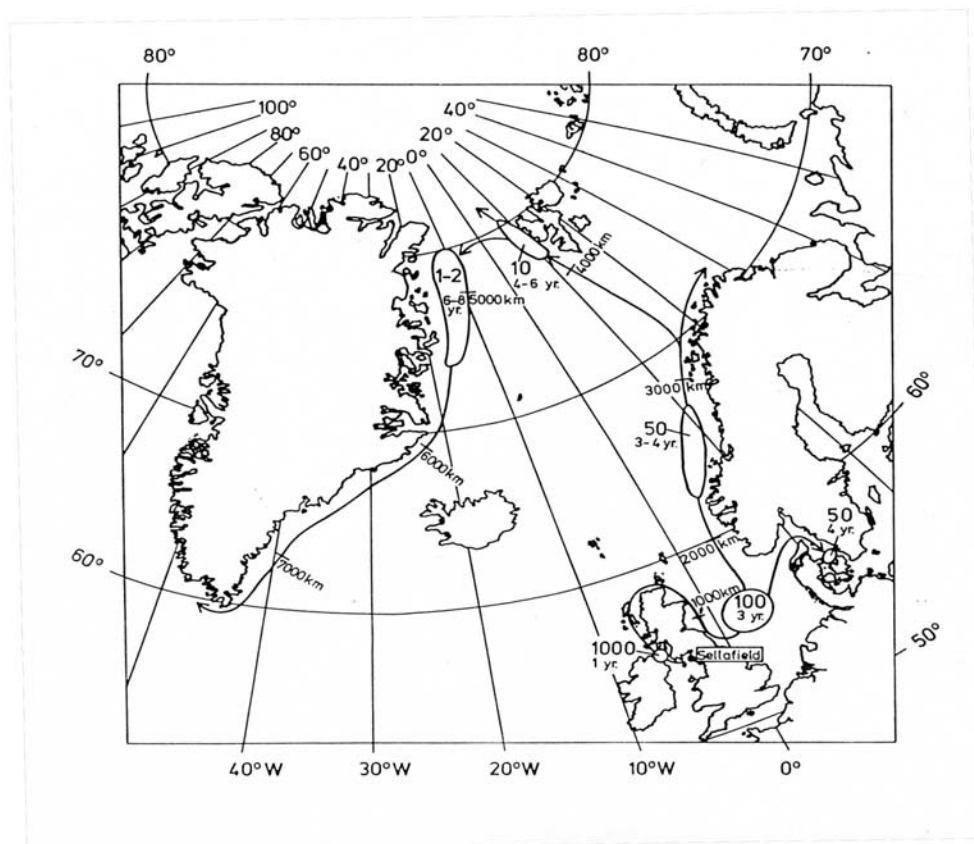


Fig. 2. The famous picture by Henning Dahlgaard on the transport of radionuclides in the North Atlantic. Relative concentrations from the source and transport time.

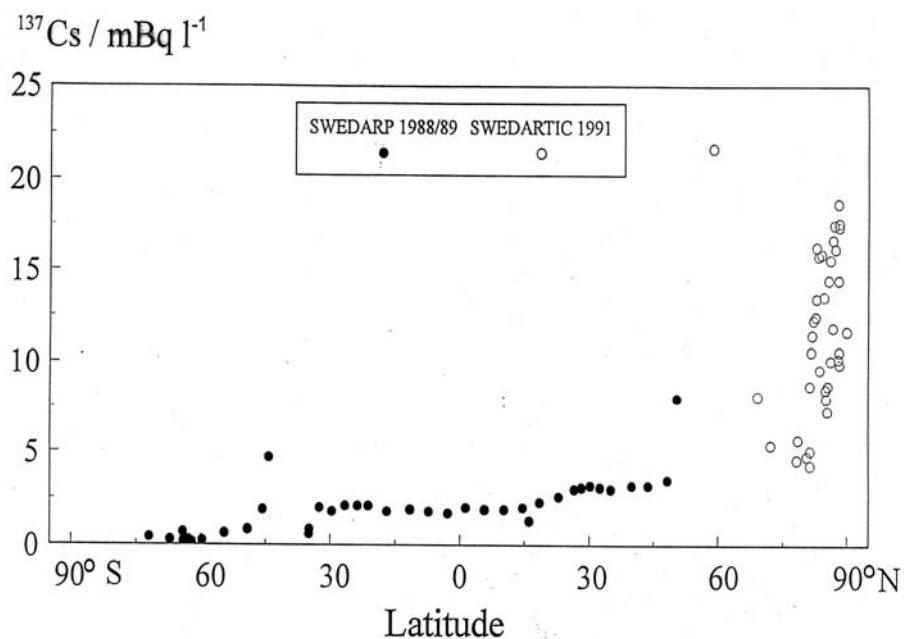


Fig. 3. Surface water concentrations of ^{137}Cs in the North and South Atlantic.

The 1990ies

Part of this decade was rather difficult for research in radioecology in some Nordic countries. The research councils did not want to give money for research related to radiation protection. To some extent this was compensated by funds from the European Union but also involved much more of administration/bureaucracy.

Good things were that mass spectrometry developed and it was easier to study isotopes such as ^{237}Np , ^{129}I and plutonium isotopes. There was also a stronger focus on chemico/physico form of elements. The modelling had an important place. There was paid more attention to areas such as NORM (Natural Occurring Radioactive Material) and TENORM (Technologically Enhanced Natural Occurring Material).

Into the New Millennium

During the last years the European Union did not support projects but rather co-ordination. Also NKS had less funding for research projects. Some people stated that we now knew everything in radioecology, we only had to sit down together and write down our knowledge.

The Universities have less money or may be spending the money on other things than free research. New analytical methods became available also non-radiometric for example to study hot particles. Investigations related to doses to the environment became an issue i.e. if there were any animals, plants which in a certain radiological situation could become endangered.

Most important is however that finally the decision makers realised that the knowledge was about to disappear if not a new young generation of scientist was created. Maintain competence and even competence building is now important within radioecology, radiochemistry and radiation biology. Emergency preparedness (in case of accidents or terrorist attacks with radioactivity) together with this competence has become the most important tool for continue radioecological research. This research is however very applied and we must fight for independent free research. The best research is often done without directives and the ideas and most interesting results appear by pure chance or mistake. A new 7th Framework programme with EU has recently been announced including Radioecology.

Some statements

from A Random Walk in Science, R.L. Weber, (Ed. E. Mendoza), The Institute of Physics, London/Bristol, 1973 (instead of references).

“I am tired of all this thing called science here. We have spent millions in that sort of thing for the last few years, and it is time it should be stopped” (Senator Simon Cameron, 1901).

I think it was Einstein who said: *“If we knew what we were doing it would not be science”*.

“If Government Laboratories had been operating in the Stone Age we should have wonderful stone axes but no-one would have discovered metals” (J. J. Thomson, 1965).

About the Atomic bomb: *“That is the biggest fool thing we have ever done. The bomb will never go off, and I speak as an expert in explosives” (Adm. W. Leahy to President Truman, 1945).*

“California constantly emits neutrons, which strike other materials and make them radioactive” (Birmingham News)

“One humiliating thing about science is that it is gradually filling our homes with appliances smarter than we are” (Anonymous).

“The demonstration that no possible combination of known substances, known form of machinery and known forms of force, can be united in a practical machine by which man can fly long distances through the air, seems to the writer as complete as it is possible for the demonstration and physical fact to be” (S. Newcomb (1835-1909)

Five Decades of Nordic Radioecology

Elis Holm
Department of Medical Radiation
Physics, Lund University, Sweden/
Centro Nacional de Aceleradores,
Seville, Spain

The 1950ies

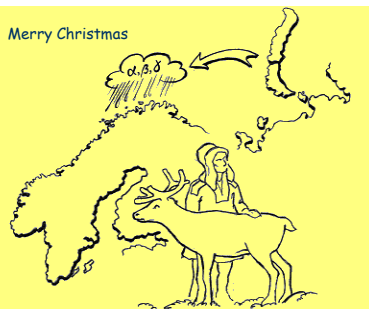
- (First nuclear tests, 1940ies + Hiroshima, Nagasaki)
- Windscale accident 1957. Release of ^{131}I
- People from Bergen were sent to Lund for whole body counting.
- ^{131}I was found but also ^{137}Cs
- During the same time several nuclear tests
- 250 test explosions, 92MT TNT

The 1960ies

- "Preliminary measurements made at the Radiation Physics Department in Lund of the caesium-137 content in five Norwegians indicated that Norwegian inhabitants could have higher body-burdens than those reported for people elsewhere" (Nature, 1961)
- New group of Norwegians from Bergen and Oslo were measured
- Norwegians were different to other people??
- Large consumption of Goat cheese???
- Body burdens were correlated to the consumption of goat cheese and milk.

- People from Kautokeino (northern Norway) were sent to Lund.
- No ^{131}I was found but very high amounts of ^{137}Cs .
- It was found out that the main reason for the bodyburdens of ^{137}Cs was reindeer meat
- **This was the birth of radioecology**

Picture stolen from some Norwegian document (Note the absence of Denmark and Iceland)



- Intensive research on the food chain lichen-reindeer- man started in Sweden, Norway, Finland, Russia and Canada.
- Also other radionuclides such as ^{90}Sr , ^{55}Fe , ^{210}Po , ^{210}Pb were investigated.
- Radiochemistry developed
- Semiconductor detectors became available (Ge(Li), Si-surface barrier)

- In 1962 Lidén stated
- "Att den radioaktiva nedskräpningen av vår jord inte får tillåtas fortsätta i samma takt som hitintills, är något som jordens alla folk genom saklig upplysning måste övertygas om. Det begränsade utrymmet för ett strålningstillskott utöver den naturliga strålningen, ett tillskott, som vi är beredda att acceptera, måste reserveras för medicinska och tekniska användningar av joniserande strålning i avsikt att förbättra vår hälsa och våra levnadsvillkor".

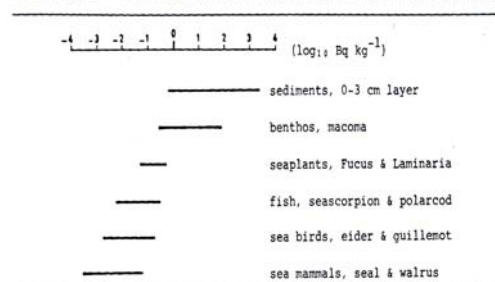
- In 1966 most states agreed to not conduct any further atmospheric tests.
- The same year the first large International congress was held in Stockholm: Radioecological Concentration Processes
- May be this is why the reserach field got the name
- Radioecology

- Well known persons attended this Symosium such as:
- **Aarkrog, Miettinen, Lidén, Jaakkola, Hanson, Kirchmann, Myttenaere, Grauby, Preston, Polikarpov, Whicker, Bouvard, Alexahin, Persson, Ramzaev, Lindell, Beasley, Salo, Kečkeš, Agnedal, Paakkola**
- Many of those people became leading in the field of Radioecology the next 20 years

- 1966 the Palomares accident, loss of nuclear weapons
- 1968 the Thule accident, loss of nuclear weapons
- This initiated the study of transuranium elements, especially Pu-isotopes and later also ^{241}Am
- Radiochemistry for these elements was developed and alpha spectrometry was improved
- Studies of Thule and Palomares still continue today
- Sea bed disposal as an option for radioactive waste (IAEA-ILMR, later MEL)

Thule results

..... Range of $^{239,240}\text{Pu}$ in Bq kg^{-1} dry matter in environmental samples collected at Thule in Aug. 1979



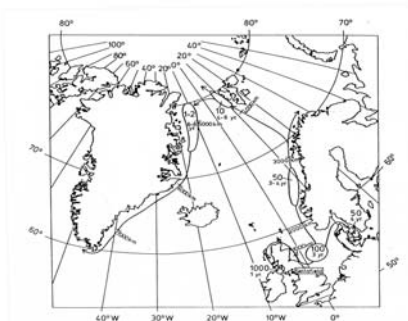
The 1970ies

- Nuclear power was built out in Sweden and Finland
- Studies around the plants showed activation products in macro algae
- Increased interest for the sea and agricultural radioecology.
- No large interest for fresh water systems until after 1986.
- Several of the first important dissertations in the field
- 1972 the London dumping convention
- Still no close collaboration between Radioecologists and "real" Ecologists
- Reasons? Radioecology was "found" by radiation physicists and Radiochemists. Those were often pro nuclear and ecologist against nuclear power.

The 1980ies

- The 1980ies the most spectacular decade of radioecology.
- The discovery of the impact from European reprocessing facilities (YMER -80 expedition) followed by several other expeditions
- NRPA, Norway did not believe in the results (they "would never start any such radio-ecological research in Norway", "the people in Lund should make a statement in the newspapers that the data were wrong"-The Chernobyl accident changed that opinion)
- Radionuclides as tracers for oceanographic and geo-chemical processes, $^{134}\text{Cs}/^{137}\text{Cs}$, ^{99}Tc

The transport of radionuclides from Sellafield in the North Atlantic in time and space (Dahlgard)

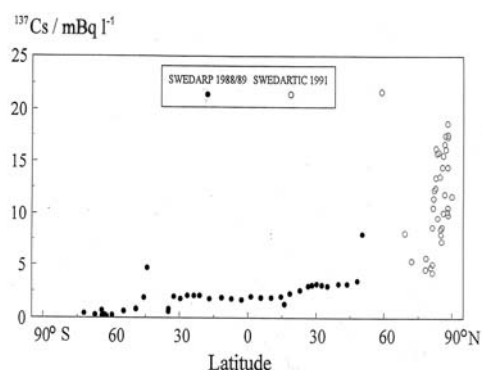


- 1986-The Chernobyl accident
- Good or bad for radioecological research?
- Good:
 - More people involved in radioecology
 - Intensive radioecology restarted in Norway
 - Other radionuclides than ^{90}Sr and ^{137}Cs could be studied
 - Start of hot-particle investigations
 - New money in the field
 - Start of reserch in fresh water ecosystems

- Bad:
 - Bad for nuclear power industry
 - Difficult for other approaches of radioecology, tracers for geochemical processes etc.
 - Too much focus on ^{137}Cs
 - After some years decreased interest for Radioecology.
 - Showed that the models were wrong
 - Do we need accidents to motivate research? Does something has to be dangerous to motivate research? Of course generally not, but for Radioecology it looks like that.

The 1990ies

- Difficult period to get research money from Research councils (anyway in Sweden)
- To some extent compensated by EU funding
- Remedial action projects
- Increased interest for the Arctic/Antarctic
- NORM and TENORM studies
- Development of mass spectrometry-analysis of Pu-isotopes, ^{129}I , ^{237}Np



The new millennium

- Statements such as: *"We now know everything in Radioecology"*
- Only co-ordination, no projects, EU and also NKS
- Doses to the environment
- Studies of radionuclide chemico-physical forms
- Hot particle studies (TIMS, SIMS, AMS etc)

- Emergency preparedness(terrorist attacks, dirty bombs, now ^{210}Po)
- Maintain competence and competence building. We need new young people in Radioecology.
- 7th framework of EU is upcoming

The future

- Independent free research, free from politics, must be re- established
- The best projects/findings are results of pure chance or a mistake (the start of radioecology, the impact from reprocessing facilities, radiocaesium in the forest industry etc..)
- International collaboration even more important
- New techniques

The AMS in Seville



Merry Christmas and a Radiant New Year.



**NKS-B YoungRad
Helsinki, 14 – 15 December 2006**

**NKS: Supporting
Five decades of Nordic Radioecology
What now?**

**Sigurður Emil Pálsson,
Programme manager, NKS-B**

Main parts of presentation

- The NKS and its structure
- The work done within NKS (past, present, future?)

The NKS

Has supported for decades Nordic co-operation in research and development within

- radiological emergency preparedness
- radioecology
- nuclear technology and safety

For more information on the NKS:

<http://www.nks.org/>

and the book "Half a Century of Nordic Nuclear Co-operation" by Franz R. Marcus (formal co-operation began in 1957).

To keep in mind concerning NKS

1. NKS is **not an institution**, it is a **voluntary co-operation** of Nordic authorities dealing with nuclear and radiological safety – they contribute to the co-operation of their own funding
2. **Every one of them** must be able to justify the usefulness of spending their funding this way.
3. The Programme manager as a salesman or negotiator!
4. Even though the official framework may not change, it is a constantly evolving environment, both for the participants and the NKS Board.
5. Revision of structure and content is ongoing.
6. **The Board is pleased with the work that has been supported (money well spent)**

The current NKS framework

- Previously the work has been organised in programme periods, each usually lasting for 4 years.
- Beginning in 2002, a different structure adopted.
- No fixed programme periods
- Two main programmes, NKS-B and NKS-R
- Proposals for activities (projects) are sent to the respective programme managers, they arrange evaluations, compile results and make recommendations to the NKS Board, which makes the final decision on activities to be supported.
- The time frame proposed can be short or long, but funding is only given year at a time

Aim (as stated in 2002, being reviewed)

"The aim with the NKS-B programme is to **strengthen radiological emergency preparedness in the Nordic countries**. Apart from activities directly targeted on emergency preparedness this also includes activities in related areas such as **radioecology and effective communication and information management**. Also these activities must, however, be focused on emergency preparedness related questions"

Now: Increased emphasis on maintaining competence in radioecology

Priorities (as defined in 2002):

Two main aspects are given highest priority:

- Maintaining and building up **competence**
(Now: increased awareness of the importance of engaging young scientists in NKS work)
- Maintaining and building **close informal Nordic networks** between scientists as well as authority officials in emergency preparedness related disciplines.

The 3 basic fields (instruments)

- **Studies** (including research, investigations, exercises etc.) focusing on maintaining and building up competence
- **Seminars** (considered to have been a very important and successful tool) aiming and building up and maintaining both competence and networks
- **Education** helping building competence in the individual countries with the aim of reaching the common goal, a better emergency preparedness in the Nordic countries

Programme content, main themes

Potential activities should fall into any of the following 3 main themes:

- **Emergency preparedness** - in general and specific tools
- **Measurement strategy, technology and quality assurance**
- **Radioecological studies** of relevance for emergency preparedness (widening the scope formally is being discussed)

Evaluation of proposals

The evaluation process involves assessing e.g.:

- how well the proposal falls within the defined **NKS-B framework**
- building-up of **competence** and maintaining it in the future
- **value for co-operation of the Nordic authorities**, including NKS criteria
- **potential use** of results and information - demonstration of interest by potential end-users and authorities is an advantage
- the **scientific and pedagogical merits** of the proposal

Process of selecting proposals for funding

- Call for proposals
- Proposals for activities sent out to an evaluation group
- Each evaluator gives each proposal a rating (1-5) + comments for explanation
- Programme Manager compiles the evaluations, gives a recommendation on how funding could be distributed based on the evaluation and total budget, taking into account the resulting distributing of funding.
- **The NKS Board decides the funding**, based on the proposals, individual evaluations and the evaluation compilation

Activities supported by NKS-B

What has been done within NKS?

- In previous periods:
 - Research (reports)
 - Seminars
 - Courses
 - Books
- Reports from current period: NKS web site <http://www.nks.org/> (25 reports within NKS-B)
- The new (to be released) **NKS DVD**
 - Contains many (258) scientific reports + other reports (including the book "Half a Century of Nordic Nuclear Co-operation" by Franz R. Marcus)
 - The reports are **fully searchable**, a valuable resource of information on what has been done and how within the NKS

Ongoing activities (1/3)

- **EMARAD**
Concluded apart from: Material from the seminar on Malicious use of radioactive material, Stockholm, May 2005, is being processed for publication on a special CD.
- **MetNet**
Nordic network of meteorological services engaged in nuclear emergency preparedness
- **BioDos**
Biodosimetry application in emergency preparedness
- **UGS**
Urban gamma spectrometry data processing

Ongoing activities (2/3)

- **URBHAND**
Decision support handbook for remediation of contaminated inhabited areas
- **YoungRad**
Seminar for young scientists in the fields of radiochemistry, radioecology and radiation protection
- **LUCIA**
Assessing the impact of releases of radionuclides into sewage systems in urban environment - simulation, modeling and experimental studies
- **ECODOSES**
Improving radiological assessments of doses to humans from terrestrial

Ongoing activities (3/3)

- **HOT**
Detection, isolation, characterization and radiochemical techniques for 'hot' particles in the environment
- **FOREST**
Guidance for sampling in forests for radionuclide analysis and update of the Nordic forest radioecology network
- **NORDRISK**
Nuclear risk from atmospheric dispersion in Northern Europe
- **REIN**
Regional differences in reindeer radiocaesium contamination

Seminars:

Open NKS-B seminars and meetings held last year (2005)

- NKS-B Seminar on Malicious Use of Radioactive Material (May 24 – 25)
- NKS-B CommTech Seminar on communication (technology) for nuclear and radiological emergency preparedness May 31 – June 1
- NKS-B Seminar on Theory of Sampling (TOS)
- NKS-B Summary Seminar, Tartu, October (with focus on radioecology and measurement techniques)
- NKS-B IRADES Course on internal dosimetry

This year (2006)

Main event: A seminar summarising work within the NKS programme as a whole since 2002, Otnäs, Finland, May 2006

YoungRad!

(+ seminar within activities)

Next year (2007)

NKS-B seminar in May 2006, where results of ongoing activities can be presented and suggestions for new activities could be presented and discussed. It is hoped that it can also act as a forum for establishing groups that will submit proposals for new activities in 2008 (to be submitted to the Board meeting in November 2007).

A recipe for a successful application

There are no simple recipes!

- Write a clear application (aim, who will be doing what, at what time, at what cost and what will be the outcome)
- Describe relevance (why should this be done)
- Describe use (are there potential end-users? If so, show that they are interested in that the work should be carried out)
- Nordic element
- Young scientists! Increase/maintain competence

(continued)

A recipe for a successful application (continued)

- Often applications are based on ongoing work in the individual countries, the NKS funding is used to give it a joint Nordic dimension
- Members of the Board need to justify nationally why NKS work should be supported, national priorities can differ between the Nordic countries
- Understanding (support) by members of the Board (especially in the country of the co-ordinator)

Don't ask what the NKS can do for you

Ask how you can contribute in such a way to the Nordic co-operation, that the Board can justify supporting your proposal...

... and you will be rewarded
(hopefully, and if not, please try again, this is an iterative process)

Thank you and wishing you a successful Nordic co-operation!

SESSION I

Nuclear Fuel and Waste

Oral presentations

Andreas Knutsson

Radionuclide Sorption onto Biofilm Covered Apatite and Quartz Minerals

Åsa Magnusson

Carbon-14 Production in Nuclear Reactors – Waste Arisings and Disposal Problematics

Joachim Holm

Ruthenium Behaviour under Severe Accident Conditions in Boiling Water Reactors

Kristin Fure, J. K. Liverud

An Automated System for Performing two Dimensional Gamma Spectroscopy Measurements of Fuel Rods

Risto Koivula

Selective Removal of Radionuclides from Nuclear Waste Effluents Using Inorganic Ion Exchangers

Ulrika Backman, A. Auvinen, J. Jokiniemi, Teemu Kärkelä, M. Lipponen, U. Tapper, R. Zilliacus, T. Kekki

Ruthenium Behaviour in High Temperature Oxidising Conditions

Poster presentations

Anumaija Leskinen, L. Togneri, M. Siitari-Kauppi, U. Alanso, M. Garcia-Gutierrez, T. Missana, A. Patelli

Determination of Granites' Mineral Specific Porosities by PMMA Method and FESEM/EDAX

Jarkko Kyllönen, M. Hakanen, A. Lindberg

Sorption of Cs to Biotite

Laura Togneri, M. Siitari-Kauppi

Radioactivity Distribution Analysis with Digital Autoradiography at HYRL

Maarit Kelokaski, T. Lähdemäki, L. Togneri, P. Hölttä, A. Möri, C. Biggin, W. Kickmaier, K.-H. Hellmuth, M. Siitari-Kauppi

Visualisation of Conductive Pore Space by ¹⁴C-PMMA Impregnation – Development Work for In Situ Studies



Radionuclide sorption onto biofilm covered apatite and quartz minerals

Andreas Knutsson

Chalmers University of Technology

Microbes are present in deep subsurface environments and it is important to include them in assessments of radioactive disposals. At repository depth there is important microbial life which may reduce the adsorption capacity of the rock surface by forming a barrier between the host rock and the groundwater.

The purpose of this study is to determine the effect of in situ grown biofilms on the adsorption of radionuclides (thorium, americium, cobalt and cesium) onto apatite and quartz mineral slides. At the Microbe site in Äspö Hard Rock Laboratory biofilms were grown in situ on the mineral slides in a high pressure flow cell in order to mimic underground repository conditions. Three kinds of slides (apatite, quartz and glass) were inserted into the flow cell providing a total surface area of 528 cm² for attachment and growth of biofilms.

Groundwater was circulated from a borehole which intersects a hydraulically conductive fracture zone via PEEK tubing and PVDF plastic without metal contact. The flow rate was 30 mL/min at ambient temperature and pressure (17 °C and 30 bars). After development of biofilms on the slides, the flow cell was sealed with valves in both ends and transported to Nuclear Chemistry, Chalmers University of Technology. The mineral slides were transferred from the flow cell to the tubes inside a glove-box with an N₂ / H₂ (97 / 3 %) atmosphere and a copper catalyst to reduce oxygen. The radionuclides used are ²³⁴Th(IV), ²⁴¹Am(III), ⁶⁰Co(II) and ¹³⁴Cs(I). Afterwards 50 mL of synthetic groundwater and 300-500 µL of radionuclide stock solutions were added to each tube and the pH was adjusted to approximately 7 in all samples and controls. The synthetic groundwater used in the experiments has a composition similar to the borehole from which the water circulating through the flow cell was taken.

The distribution coefficients, K_d, are determined from measurements of the distribution of trace elements between the mineral slides and the synthetic groundwater.

The activities remaining in solution are measured using a liquid scintillation counter or a HPGe detector. The sorption to the rock slides are analyzed by autoradiography. Biofilms are characterized before and after the sorption experiments using microscopy. This work is performed within FUNMIG, a four year (2005-2008) joint European research project with focus on raising the fundamental understanding of radionuclide migration processes and implements this knowledge into the ongoing work of planning and building deep geologic high-level nuclear waste repositories.

Name	Andreas Knutsson
Company / University	Chalmers University of Technology
Web-page	www.chalmers.se
Phone (direct line)	+46 31 772 2914
Fax	+46 31 772 2931
E-mail	andreas.knutsson@chalmers.se

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Radionuclide sorption onto biofilm covered apatite and quartz minerals

Andreas Knutsson

Nuclear Chemistry
Dept. of Chemical and Biological Engineering
Göteborg, Sweden

CHALMERS Chalmers University of Technology

Handling of spent nuclear fuel

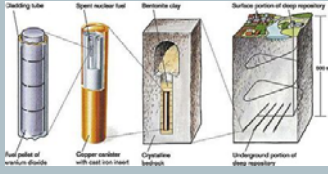
- Sweden has alongside with other nations like Finland, Canada and USA adapted to the once through fuel cycle:

The residual fissile and fertile content of the spent fuel and other fission products are to be considered as waste for geologic disposal and not put in to further good use
- Confinement periods up to 100 000 years
- Repositories located deep underground in appropriate geological formations

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Barriers

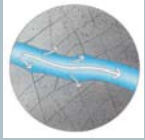
- Ground water fluxes are considered the most important transport mechanism that can result in release of radionuclides into the biosphere
- A barrier system is designed to prevent or at least delay the release of potential hazardous radionuclides from the repository
- Multi-barrier system (KBS-3)**
 - The nature of the fuel/waste matrix itself
 - The canisters/cladding
 - Bentonite clay buffer
 - Host-rock



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The Swedish host-rock

- Granite bedrock in the Fennoscandian shield
- Fennoscandian shield is 1.6-3.1 billion years old and has been fractured by considerable forces during glaciations within that time span
- Fractures at an overall average of 2 meters with significant local variations
- Hydraulically conductive fractures
 - Radionuclide adsorption at fluid-rock interface
 - Radionuclide transport dissolved in ground water or via suspended colloids



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Microorganisms

- Everywhere in nature
- Can as a group extract energy from virtually any exothermic redox-reaction
- Subsurface microbiology

Number of procaryotes probably exceeds the number of other components found in the biosphere
- Since the 80s microbiology has been a part of the Swedish program for radioactive waste disposal for their potential effect on the performance of nuclear waste repositories

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Production of biofilm

- Fennoscandian shield groundwaters:**
 - $10^5 - 10^6$ cells mL^{-1}
 - surface attached or planktonic
- Microbes are not only present in subsurface environments they are also active
 - Any solid surface immersed in a water phase with living microbes is predestined to develop biofilms
- A accurate representation of the environment for the migrating radionuclides are hence biofilm covered fracture surfaces which will alter the sorption behaviour of the host-rock

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Question

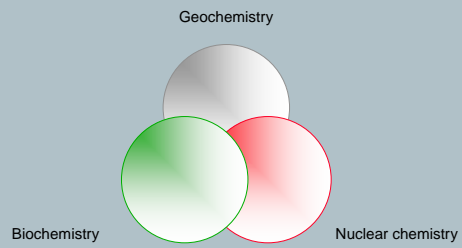
- Microbes in biofilm
 - Immobilizing or mobilizing?



The purpose of this study is to determine the effect of *in situ* grown biofilms on the adsorption of radionuclides onto apatite and quartz mineral slides

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Combination of sciences



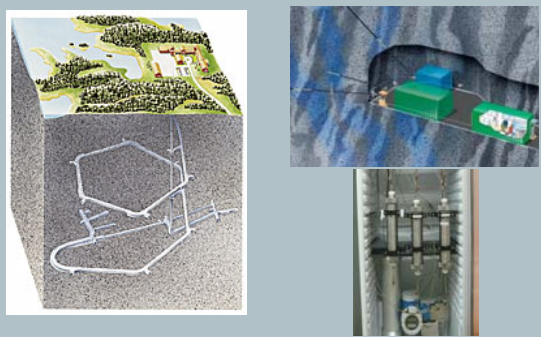
Geochemistry

Biochemistry

Nuclear chemistry

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Experimental approach

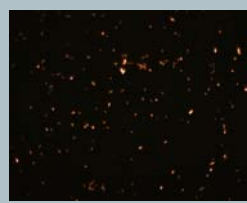


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Microscopy snapshot


Dominating species

- sulphate reducing bacteria,
- methanogens
- acetogens



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Sorption experiments



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Sorption experiments

Radionuclides

$^{234}\text{Th(IV)}$
 $^{241}\text{Am(III)}$
 $^{60}\text{Co(II)}$
 $^{134}\text{Cs(I)}$

Surfaces

- 1) **apatite**– biofilm on apatite
- 2) **quartz**– biofilm on quartz
- 3) **glass**– biofilm on glass
- 4) blank
- 5) acid reference



(* With attached biofilm)

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Analysis methods

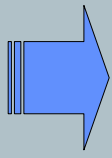
- *LSC/HPGe*
- *Autoradiography*
- *Electronic microscopy/Cell counting/TOC*

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Result to date


Depending on the radionuclide investigated the subsurface adsorption onto granite is positively or negatively affected by biofilms

- $^{60}\text{Co(II)}$
- $^{241}\text{Am(III)}$
- $^{234}\text{Th(IV)}$
- $^{237}\text{Np(V)}$
- $^{99}\text{Mo(VI)}$



12-88 % Higher adsorption for granite

- $^{147}\text{Pm(III)}$



57 % Higher adsorption for biofilms

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Acknowledgements





Svensk Kärnbränslehantering AB

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FUNMIG

- FUNMIG is a four-year (2005-2008) Integrated Project under the Sixth Framework Programme of the EC
- Main objectives of FUNMIG are the fundamental understanding of radionuclide migration processes in the geosphere, especially focused on tools for application to performance assessment



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Thanks for your attention!



Waste arisings and local environmental effects caused by ^{14}C production in various types of nuclear reactors

Åsa Magnusson

Lund University, Department of Physics, Division of Nuclear Physics, P.O. Box 118, SE-221 00 Lund, Sweden

Carbon-14 is a radionuclide ($T_{1/2}=5730$ years) that is produced in all types of nuclear reactors mainly through neutron-induced reactions with ^{17}O , present in the reactor coolant. The production generates a variety of gaseous, solid and liquid waste.

According to UNSCEAR, the main contribution to the global dose from radionuclides released in various stages of the nuclear fuel cycle is from globally dispersed ^{14}C . Also the collective effective dose from low- and intermediate-level disposal of nuclear waste is almost entirely due to ^{14}C . Therefore increased knowledge of the behavior of ^{14}C inside the power plant (chemically and physically) and of the release paths is essential. This to be able to control the release of ^{14}C to the environment by the use of appropriate waste management strategies and practices.

The direct ^{14}C releases from nuclear power plants are dominated by gaseous emissions, mainly as $^{14}\text{CO}_2$. Due to incorporation of $^{14}\text{CO}_2$ in plants by photosynthesis, increased ^{14}C levels may be found in the surrounding terrestrial environment. The excess ^{14}C will eventually reach humans through food ingestion, which is the main pathway for ^{14}C intake by humans. Measurements of the ^{14}C in environmental samples are therefore important for estimates of radiation exposure to the public.

Waste arisings and local environmental effects caused by the production and release of ^{14}C from nuclear reactors are presented. The studies include the most common reactors in the world: Pressurized Water Reactors (PWR), Boiling Water Reactors (BWR), CANDU- and RBMK reactors. Terrestrial as well as aquatic samples from the vicinities of BWRs, CANDUs and RBMK showed that CANDU reactors, followed by the investigated RBMK, had the most significant effect on the ^{14}C levels in the surrounding environment.

The indirect ^{14}C releases from power reactors comprise different types of deposited solid waste containing ^{14}C , which can be released from the repository with a potential future impact on human health. Operational waste from Swedish reactors is deposited in the repository for radioactive operational waste, called SFR. The dominating type of waste in SFR is spent ion exchange resins which are used to clean e.g. reactor water. ^{14}C dominates the total dose for the SFR in most future release scenarios. The ^{14}C inventory- on which the dose calculations are based- has previously been estimated using scaling factors, i.e. theoretical estimations. To decrease the uncertainty of the estimated ^{14}C inventory, direct measurements of the resins are required. To perform these analyses, sample specific ^{14}C extraction methods were developed to analyze spent resins, process water and gas samples from Swedish PWRs and BWRs.

The results showed that the PWR resins have the highest ^{14}C concentrations; they accumulate up to 9% of ^{14}C produced in the reactor coolant. The total ^{14}C activity accumulated in spent resins from Swedish reactors during their life-time, i.e. the total ^{14}C inventory in SFR, was estimated to be 5 TBq. The analyses also showed that estimations using fixed scaling factors are very uncertain and can result in the total ^{14}C inventory being underestimated.

Name	Åsa Magnusson
Company / University	Lund University
Web-page	http://nuclearphysics.nuclear.lu.se/
Phone (direct line)	+46 46 222 77 33
E-mail	asa.magnusson@nuclear.lu.se

Carbon-14 production in nuclear reactors – Waste arisings and disposal problematics

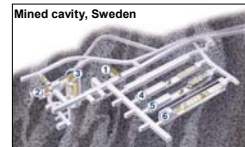


Åsa Magnusson
Department of Nuclear Physics,
Lund University



Background

- Nuclear power industry
 - 442 reactors and increasing...
 - 33 different countries
- Waste generation
 - Very Low-Level Waste (VLLW)
 - Low-Level Waste (LLW)
 - Intermediate-Level Waste (ILW)
 - High-Level Waste (HLW)
- Disposal
 - VLLW, at plant site
 - LLW/ILW, at joint facilities
 - HLW, no existing facilities today



Disposal of LLW-ILW

Worldwide

- More than 100 disposal facilities
- 80% are near-surface facilities
 - Simple near-surface facilities (SNSF), US
 - Engineered SNSF, UK
- Mined cavities (MC), Sweden, Finland, Norway
- Geological repositories, Germany



Sweden

- SFR = Final repository for radioactive operational waste
- SFR operated by SKB (Swedish Nuclear Fuel and Waste Management Co.)
- Dominating waste type in SFR: spent ion exchange resins
- Future doses from SFR dominated by: ^{14}C



Despite this- ^{14}C content in waste NOT measured (~2004)
2004–2007: Lund University performs ^{14}C analysis

Carbon-14

- Main contributor to the global dose from radionuclides released from the nuclear power industry (UNSCEAR)
- Dominates the collective dose from LLW-ILW disposal facilities (UNSCEAR)

Why?

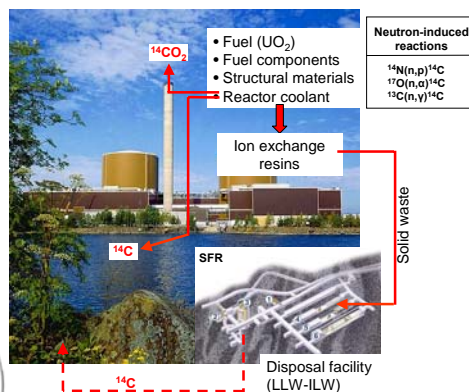
- Long half-life (5730 years)
- High mobility in the environment
- ^{14}C enters the natural carbon cycle → becomes a part of the food chain → gives an additional radioactive dose to humans

Minimizing ^{14}C both in waste and in releases from the power plant IMPORTANT!

But:

- Low energy beta emitter → Difficult to measure
- Limited knowledge
- Difficulties selecting appropriate waste management strategies

^{14}C Production and releases



Analysis of ^{14}C in nuclear waste

Problem

- Low energy beta-emitter
- High gamma activity in waste samples

BUT:

- ^{14}C might be present as both inorganic and organic compounds
- Spent resins – organic ^{14}C of greatest interest
- Reactor water – both fractions (individually!) of interest

Developed methods



Solution

- Separate ^{14}C from the waste by $^{14}\text{CO}_2$ formation → Absorb $^{14}\text{CO}_2$ in alkaline solution → Measure A by LSC
- Method with low detection limit, permitting small subsamples
- Method that extracts both fractions
- Develop method that quantifies both fractions separately!

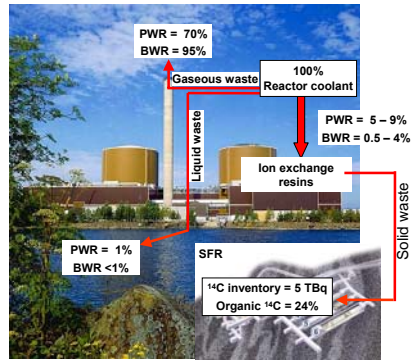
Results

Study included:

- 3 PWRs (Sweden)
- 6 BWRs (Sweden)

Sampling of:

- Spent resins
- Process water
- Off-gas





Chemistry under severe accidents

Joachim Holm

Chalmers University of Technology

Chalmers have worked with the chemistry under severe accidents in a Nuclear Power Plant (BWR) for about a decade. Chalmers have especially looked at the behaviour of the hazardous fission product iodine, in different forms, under a severe accident. Among other things the interactions between iodine and several metals like aluminium, zinc and copper have been investigated.

Another fission product that will cause problems if it is released from the reactor is ruthenium. The fission product is accumulated in fuel during regular operations in a nuclear power plant, but is not released from the reactor vessel even under a "normal" accident. But under an air-ingress accident ruthenium can be released out of the reactor vessel in form of the volatile species RuO_3 and RuO_4 . However, RuO_3 is only stable at high temperature and will deposit as RuO_2 .

In this project Chalmers will look at interactions between RuO_4 and some metals, like alumina, zinc and copper. All these metals are in the containment in a BWR. The quantities of the metals are 1-10 tonnes, for example at sheets and fans.

The equipment that will be used is a modification of an already existing experimental set-up, which can be seen in Glänneskog's thesis [GLÄ 05]. The experimental set-up contains of one reactor vessel, two glass loops (one for liquid phase and one for gas phase), two pumps and two NaI(Tl) detectors connected to a computer.

A method for production of RuO_4 -crystals from irradiated RuCl_3 , has been developed. The crystals are formed in a "ice-trap".

The RuO_4 -crystals will be placed in the reactor vessel. First the distribution of RuO_4 between the gas and the liquid phase will be examined. When equilibrium has been established, a metal sample of either aluminium, zinc or copper will be introduced in the reactor vessel. The metal samples will later on be investigated with the SEM and ESCA techniques, to see the speciation of RuO_4 .

Some first results will hopefully be presented at the seminar.

[GLÄ 05] Iodine-Metal Surface Interactions under Severe Accident Conditions in a Nuclear Power Plant, H. Glänneskog, PhD thesis, Chalmers University of Technology, 2005

Name	Joachim Holm
Company / University	Chalmers University of Technology
Web-page	www.chalmers.se
Phone (direct line)	+46 31 772 29 16
Fax	+46 31 772 29 31
E-mail	joachim.holm@chalmers.se

CHALMERS Nuclear Chemistry
Department of Chemical and Biological Engineering

Ruthenium Behaviour under Severe Accident Conditions in Boiling Water Reactors

Joachim Holm

CHALMERS Nuclear Chemistry
Department of Chemical and Biological Engineering

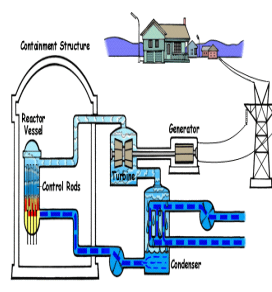
Background

- **Ruthenium**
 - ~2 kg Ru per ton spent nuclear fuel
 - Chemical toxic and radiotoxic
 - ^{103}Ru ($t_{1/2}=39.3$ d) and ^{106}Ru ($t_{1/2}=374$ d)
- **Release of ruthenium to containment**
 - RuO_x much more volatile than Ru-metal
 - RuO_4 (m.p. 25°C, b.p. 40°C)

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Background

- **BWR**
 - 7 BWRs in Sweden
- **Severe Accident**
 - Air-ingress
 - Startup/shutdown
 - RA-LOCA



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The Project

- **Reaction between metal surfaces and RuO_4**
 - Aluminium, Zinc and Copper
 - Reaction rates
- **SEM and ESCA**
 - Speciation of ruthenium
- **Distribution of $\text{RuO}_4(\text{g})$**
 - Between aqueous- and gas phase

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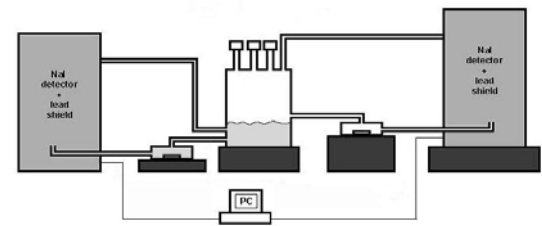
The Project

- **Metals in a BWR containment**
 - Aluminium ~ 10 tonnes¹ – Sheets and fans
 - Zinc ~ 8-10 tonnes¹ – Bars and gratings
 - Copper ~ 2 tonnes¹ – Cables

¹ Forsmark 1, Sweden

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Experimental set-up



- Temperature: 25-90 °C
- Pressure: 1 atm

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Experimental set-up

- Imitate the environment in the containment
- Volumes and metal surfaces are representative for a BWR under a severe accident

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The Project

- **Production of RuO_4**
 - Distillation
 - $\text{RuCl}_3 + \text{KMnO}_4 + \text{H}_2\text{SO}_4$
 - Crystals (?)
- **Irradiation of RuCl_3**


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Other projects

- Radiolysis of iodine in gas phase
- **Properties of CH_3I**
 - Distribution of CH_3I in neutral water solutions
 - Retention of CH_3I in $\text{Na}_2\text{S}_2\text{O}_3$ (scrubber)
- **Chloride vs Iodine**

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Department of Chemical and Biological Engineering

Questions ?





An automated system for performing two dimensional gamma spectroscopy measurements of fuel rods

Kristin Fure, Jan K. Liverud

Institute for Energy Thechnology, OECD Halden Reactor Project

Lab View is a commercially available software with a variety of opportunities. In this project, Lab View is utilized in a program that both serves as a control desk for controlling a positioning rig and for carrying out gamma spectroscopy measurements. The system is divided in two sub programs: one called "Gamma_scan_rig" and the other called "Gamma_spectrum_reader". The two sub programs user interfaces look similar, but have different options. The Gamma_scan_rig program interfaces the positioning rig and the gamma scan equipment and is used for carrying out the measurements, while the Gamma_spectrum_reader is an offline application for analysis and reporting support.

From the Gamma_scan_rig program you may move the sample in two dimensions. The coordinates of the sample according to a fixed zero point, are shown. An automatic driving path may be set in a row – column oriented manner and the measurements can then be run without human interaction. The gamma spectroscopy part enables full flexibility regarding setup of the gamma spectroscopy equipment. HV (High Voltage) on/off, enabling of pole zero and gain adjustment are among the built in features. A full spectrum of 2048 channels is shown on the screen. There are options for zooming in a smaller area of the spectrum, and it is possible to set an area, ROI (Region Of Interest), within the spectrum where a simple summation of counts is done. Compton background is estimated by making an average over three channels to each side of the ROI, and the background counts are subtracted from the summation in the ROI to make net counts. A pre set counting time may be set in so called Live Time: The time the detector is available for measuring gamma quantum. The time that the detector is occupied with a gamma quantum and is therefore not capable of measuring a new, is shown in percentage of real time elapsed. Net counts in ROI are displayed on the screen as coloured dots plotted versus horizontal and vertical position of the rig. The software is developed for measuring gamma radiation from reactor fuel rods in two dimensions or for measuring gamma radiation from so called flux wires. The diagram of coloured dots visualises the activity distribution over the fuel rod or flux wire.

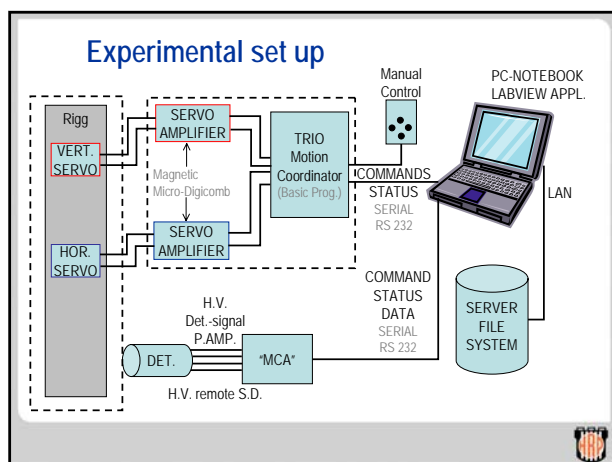
In the Gamma_spectrum_reader program the acquired data may be further analysed. Here one may calculate net peak areas that also give reliable results when peak position is at a compton edge. The uncertainty of the peak area is calculated as well as the peak's centroide. For this, common equations used in commercial gamma spectroscopy programs are used. The user also has the option to save an image of the two dimensional plot as well as peak data.

The advantage with the Gamma_scan_rig and the Gamma_spectrum_reader programs compared to using a commercial spectroscopy program in conjunction with another program for driving the rig, is that the rig and the gamma measurement are operated from one computer and one program system. In this way, the setup, sample movement and the gamma spectrums are effectively conserved in one data file and all the data are loaded directly into the Gamma_spectrum_reader program without conversions.

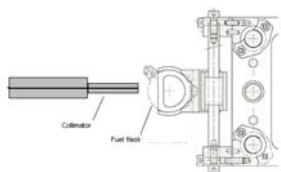
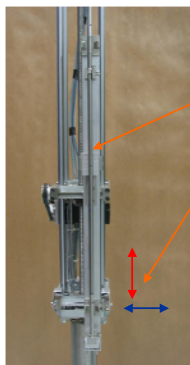
Name	Kristin Fure
Company / University	Institutt for energiteknikk, Halden
Web-page	http://www.ife.no/haldenprosjektet/hrp-no
Phone (direct line)	+47 69 21 21 83
Fax	+47 69 21 24 70
E-mail	kristinf@hrp.no

Kristin Fure
Jan K. Liverud

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- Position of fuel rod or sealed flask
- Vertical and horizontal motion



HPGe-detector

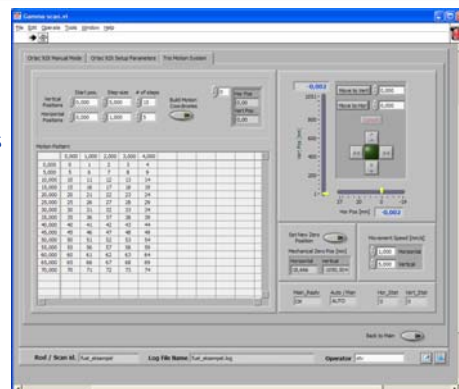
Positioning of detector when measuring:

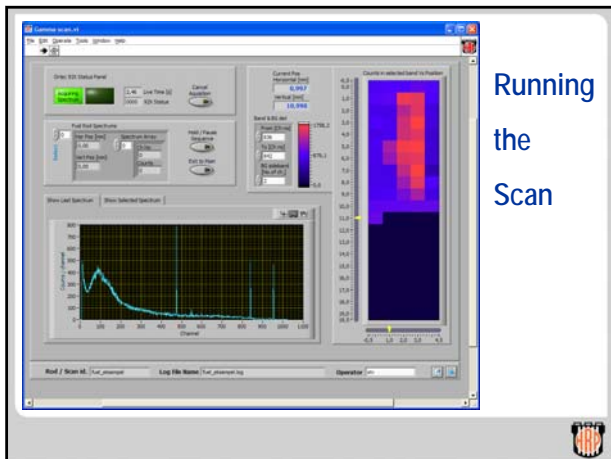
- flux wires
- fuel rods



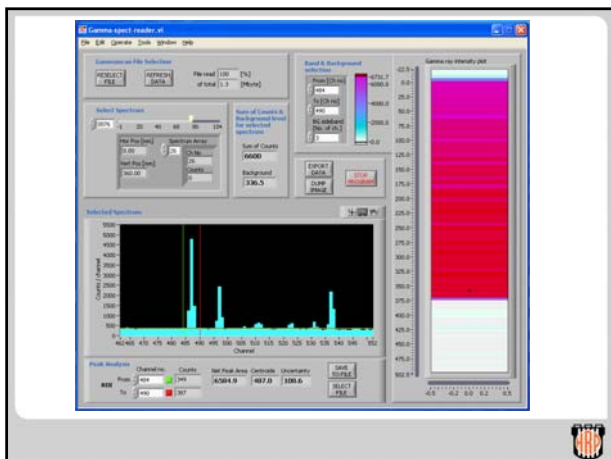
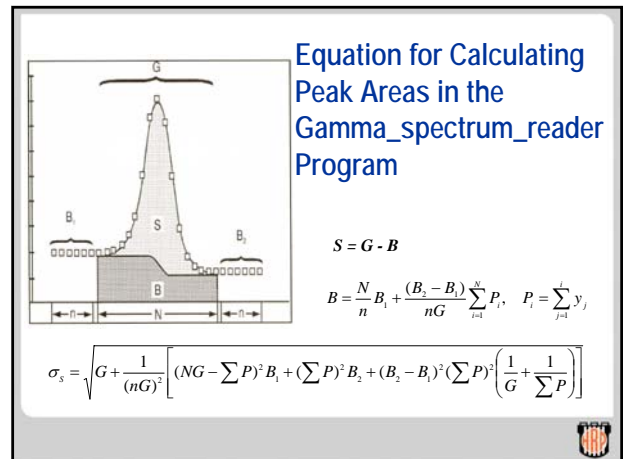
- ✓ Trio Motion Coordinator
- ✓ Servo Amplifier for vertical and horizontal motion
- ✓ Signals to and from the rig
- ✓ Signals to and from the computer and the manual control stick

Building of motion coordinates in the Gamma_scan_rig program





Running
the
Scan



From the Gamma_scan_rig program you may:

- Control MCA and Detector conditions
- Drive the rig
- Set up measurement conditions
- View spectrum
- Select ROI and view plot during measurement

In the Gamma_spectrum_reader program you may:

- View spectrum
- Select ROI and plot a simple summation of counts versus position
- Select ROI and calculate peak area, centroid and uncertainties

Questions ?



Selective sorption properties of inorganic materials

Risto Koivula

Laboratory of Radiochemistry, Department of Chemistry, University of Helsinki, P.O.Box 55, FIN-00014 Helsinki, Finland

Ion exchange materials and processes are well known and widely used separation technique in industry as well as in research laboratories. Development of ion exchange processes and materials will be on selective separation and R&D on inorganic materials for selective separation processes has been strong for several years. [1] The superior selectivity of some inorganic ion exchangers, compared to other sorption materials presently used in the separation processes, has been the major initiative for the research. High selectivity is the key to fulfil the strict regulations concerning waste effluents and enhance the energy efficiency of the separation processes.

Several selective inorganic ion exchange materials have been developed at the Laboratory of Radiochemistry for decontamination of low and intermediate radioactive waste solutions, and some of those materials have found industrial applications. One of them is extremely cesium selective material ($k_{Cs/Na}=1,500,000$), a transition metal hexacyanoferrate (CsTreat®), which is granular and has a wide operational pH range (pH 1 to 13).[2] The physical properties, such as granular form, are one of the key factors for ion exchange materials in their conventional separation processes and untypical for majority of selective inorganic materials. Also, for the second most important fission product, strontium, we have been developed a granular sodium titanate (SrTreat®) material that has high selectivity ($k_{Sr/Na}=200,000$) but rather limited pH range (above 9). Our recent studies have focused on selective separation of activated corrosion products, such as ^{60}Co and ^{63}Ni , where metal oxides with various doping elements have showed promising results. Particularly tin antimonates have showed high selectivity towards nickel and distribution coefficients as high as 7 000 ml/g in acidic solutions (0.1 M HNO_3) has been obtained [3]. Nickel is generally considered as one of the most difficult transition metal to separate from radioactive waste solutions. Doping metal oxides has clear effects on structure of the material and it's selectivity properties and so it can be used to manipulate the materials ion exchange properties [4]. Ongoing research on selective sorption of radioactive oxyanions, such as technetium ($^{99}TcO_4^-$) and ^{125}Sb , has been most promising and opening a new and highly interesting research area of selective anion exchange.

References:

1. Clearfield, A., Solv. Extr. Ion Exch., 2000, 18(4), 655.
2. Tusa, E., Paavola, A., Harjula, R. and Lehto, J., in: Proceedings of the 8th International Conference on Waste Management and Environmental Remediation, Sept. 30 – Oct. 4, 2001, Bruges, Belgium.
3. Koivula, R., Harjula, R. and Lehto, J., J.Mater.Chem., 2002, 12, 3615-3619
4. Koivula, R., Harjula, R. and Lehto, J., Separation Science and Technology, 2003, 38(15), 3795.

Name	Risto Koivula
Company / University	University of Helsinki
Web-page	www.helsinki.fi/kemia/radiokemia
Phone (direct line)	+358 9 191 50130
Fax	+358 9 191 50121
E-mail	risto.koivula@helsinki.fi

Selective removal of radionuclides from nuclear waste effluents using inorganic ion exchangers

'YOUNGRAD'
14.12.2006 Helsinki, Finland

Risto Koivula
Laboratory of Radiochemistry, University of Helsinki, Finland



Selective ion exchange

- Background
- Concept of selective ion exchange
 - What is it and why it is important
- How do we change the selectivity of materials
- Case study of selective inorganic ion exchangers
 - Treat-family
 - Their use and effectiveness
 - Metal oxides
 - Doping with metals and its effect on structure and acidity



BACKGROUND

- Laboratory of Radiochemistry, Ion Exchange Group
 - Some 4 to 8 person working for the group (so we are (or have been;) a big group even in international scale)
 - Development of new materials for removal of trace pollutants (radionuclides, heavy metals, oxo-anions)
 - First commercial material was developed (CsTreat) and taken in routine use at Loviisa NPP 1991



Selective ion exchange

- Why high selectivity?



Selective ion exchange

- Why high selectivity?

- Selectivity coefficient

$$k_{Cs/Na} = \frac{[Cs]_S [Na]_L}{[Cs]_L [Na]_S}$$

S and L refers to the equilibrium concentration in the solid and in the liquid phases, respectively



Selective ion exchange

$$k_{COND} = \frac{[Cs]_S [Na]_L}{[Cs]_L [Na]_S}$$

- Why high selectivity

- Distribution coefficient

$$k_d = \frac{[Cs]_S}{[Cs]_L}$$

maximum theoretical processing capacity

- For both static batch experiments and dynamic column experiments
- Batch experiments fast and easy
 - Estimate column performance



Selective ion exchange

Why high selectivity

$$k_d = \frac{Q}{\frac{[Na]_L}{[Cs]_L} + [Cs]_L}$$

, after inserting $[Na]_S = Q - [Cs]_S$

- Q has theoretical limit that isn't very high as in numbers
- $[Na]_L \gg [Cs]_L$
- Selectivity coefficient has no upper limit, dominates the equation

$$k_{Cs/Na} = \frac{[Cs]_S}{[Cs]_L} \frac{[Na]_L}{[Na]_S}$$

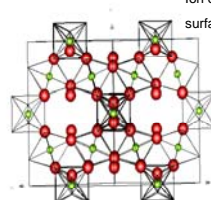
$$k_d = \frac{[Cs]_S}{[Cs]_L}$$



Selective ion exchange

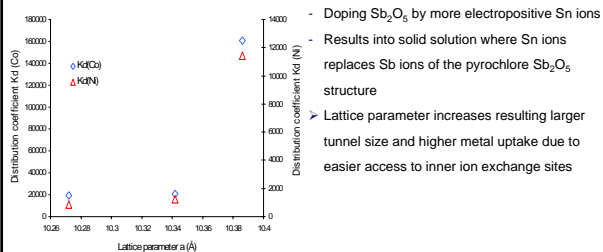
How do we 'build' selectivity

- A case study of antimony pentoxide (Sb_2O_5)
 - Has a rigid tunnel structure (pyrochlore)
 - Ion exchange sites mainly inside the structure but also on the surfaces of the material
 - Well known material for Sr uptake but calcium ions diminishes its Sr uptake properties

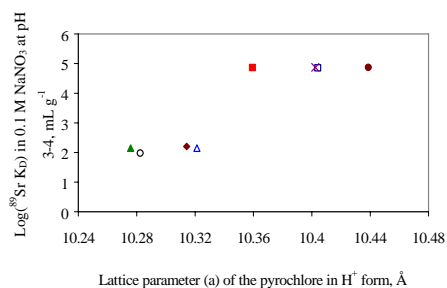


Selective ion exchange

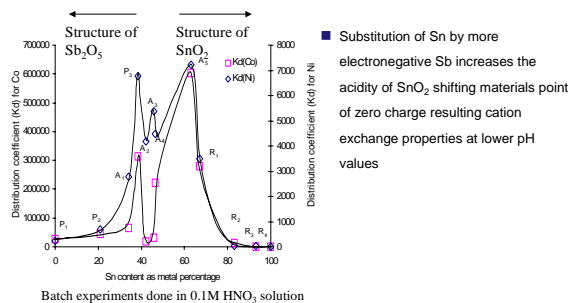
Building the selectivity



Selective ion exchange



Selective ion exchange

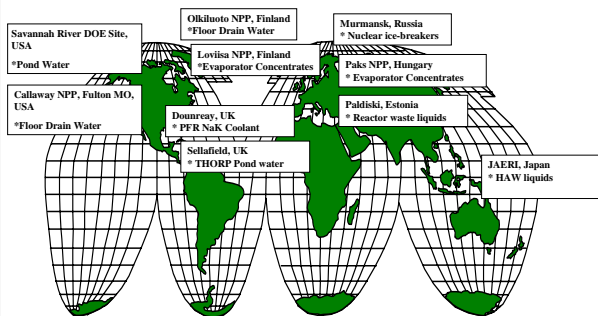


Selective ion exchange

- Treat-family: CsTreat®, SrTreat®, and CoTreat®
 - 100% inorganic
 - Granular, column capable materials available
 - All commercialized materials



Commercial Applications of CsTreat, SrTreat and CoTreat



Selective ion exchange

■ CsTreat®

■ Hexacyanoferrate

- Selectivity is originated from the tight fit of Cs on the cavities of the material
- $K_{Cs/Na}$ close to 1 500 000
- Ion exchange capacity only 0.35 meq/g
- Operation pH: 1-13 (high salt)
2-11 (low salt)



Selective ion exchange

■ SrTreat® and CoTreat®

■ Both sodium titanates

- Layered structure
- Ion exchange capacity ~5 meq/g, pH dependent
- $K_{Sr/Na}$ around 200 000



Selective ion exchange

■ CsTreat: APPLICATION OF FLOOR DRAINS

Callaway NPP, MI, USA

- * Na 100-300, Ca 20-60, K 8-23 ppm
- * 250 l (150 kg) of CsTreat
- * About 3000 m³ processed with no ionic cesium breakthrough

Olkiluoto NPP, Finland

- * 240 m³ treated with 12 liters of CsTreat
- * VRF 20,000, (VRF = Volume reduction factor)

REACTOR WATER TREATMENT

Paldiski Naval Base

- * 760 m³ of liquid treated with one 12 liter CsTreat column
- * DF was 3,000
- * VRF 63,000



Selective ion exchange

■ EVAPORATOR CONCENTRATES

LOVIISA NPP



- Before the Treatment
40-70 g/l Na, 2-10 g/l K
Cs concentration 8 µCi/l
- After the Treatment
>900 m³ (60,000 gal/cu.ft)
treated with 112 L of CsTreat
- Processing capacity 12.2 m³/kg



Selective ion exchange

■ SPENT FUEL REPROCESSING LIQUID

CsTreat and SrTreat Application in JAERI



- Before the Treatment
Cs and Sr, both 200 mCi/l
Dissolved salt 7.6 g/l
HNO₃ concentration 1.74 mol/l
- After the Treatment
Cs and Sr: DF > 1000
CsTreat loading 230 Ci/kg
SrTreat loading 170 Ci/kg



Selective ion exchange

■ POOL WATER TREATMENT

at Savannah River Site, SC, USA

Graver/Fortum System in R-Basin



Nuclide Removal and Boron
Recovery Systems of Paks NPP,
Hungary



Selective ion exchange

- Most recent research
 - Selective removal of activated corrosion products
 - Metal oxides
 - Selective removal of oxy-anions
 - Reducing materials
 - Selective electrochemical ion exchange using inorganic materials



Transport of Ruthenium in diverse oxidising conditions

Teemu Kärkelä, Ulrika Backman, Ari Auvinen, Riitta Zilliacus, Maija Lipponen, Tommi Kekki, Unto Tapper, Jorma Jokiniemi
VTT Technical Research Centre of Finland, P.O.Box 1000, FIN-02044 VTT, Finland

During routine nuclear reactor operation, ruthenium will accumulate in the fuel in relatively high concentrations. In an accident in a nuclear power plant it is possible that air gets into contact with the reactor core. In this case ruthenium can oxidise and form volatile ruthenium species, RuO_3 and RuO_4 , which can be transported into the containment. In order to estimate the amount of gaseous ruthenium species it is of interest to know, how it is formed and how it behaves.

A tubular flow reactor was used to oxidise the ruthenium source (RuO_2 powder) at high temperature. Oxygen volume fraction in experiments ranged from 6 to 21 % and furnace temperature from 1100 to 1700 K. The non-condensable gas flow through the furnace is set to 5 l/min (0°C, 101325 Pa). Water is added to the gas stream either by saturating air flow in a thermo-stated bubbler or by adding superheated steam through critical orifice directly into the gas stream.

As the gas exit the reactor, it cools down in a stainless steel tube and the gaseous ruthenium oxides decompose partly to RuO_2 particles. Aerosol particles are filtered out at point 106 cm downstream of the reactor. Gaseous RuO_4 is trapped downstream of the filter in a 1 M NaOH-water solution. At point 74 cm downstream of the reactor gas-phase sampling is done with differential mobility analyser (DMA) and condensation nucleus counter (CNC), as well as RuO_2 particles are collected on copper grids with electrostatic precipitator (ESP) and analysed with transmission electron microscope (TEM). The morphology of RuO_2 particles deposited on the surfaces of ceramic furnace tube is studied using scanning electron microscope (SEM).

Ruthenium release rate increased from 0,11 to 19,43 mg/min as temperature increased from 1100 K to 1700 K. According to results, the release rate of ruthenium decreases while the oxygen partial pressure is decreased. Increasing steam partial pressure while keeping the oxygen partial pressure constant seemed to have no effect on the release rate.

In all experiments most of the released ruthenium deposited as RuO_2 on the surfaces. The most important retention mechanism was thermal decomposition of gaseous RuO_3 , which takes place as the flow is cooled down to approximately 800°C near the outlet of the furnace. Deposition profile was measured in the experiments where RuO_2 powder sample contained gamma-active ^{103}Ru isotope.

The rate of ruthenium transported as gaseous RuO_4 into trapping bubbler ranged from ~ 0 to 0,17 mg/min. Due to very low release rate, the lowest transport rate of gaseous ruthenium was measured at 1100 K furnace temperature. The highest transport rate was measured at 1300 K. When the temperature of the furnace exceeded 1300 K, additional ruthenium deposition peak was formed in the cooler section of the stainless steel tube. This peak is probably related to catalytic decomposition of gaseous RuO_4 .

As a conclusion of the work, it can be said that if ruthenium is released from the fuel during an air ingress accident, a significant amount of it is expected to be released from the primary circuit in gaseous form. The most likely mechanism for the release of gaseous ruthenium would be revaporisation of RuO_2 particles deposited on tube surfaces.

Name	Teemu Kärkelä
Company / University	VTT Technical Research Centre of Finland
Web-page	www.vtt.fi
Phone (direct line)	+358 20 722 5718
Fax	+358 20 722 7021
E-mail	Teemu.Karkela@vtt.fi

Ruthenium behaviour in high temperature oxidising conditions

Ulrika Backman Ari Auvinen Jorma Jokiniemi
Teemu Kärkelä Maija Lipponen Unto Tapper Riitta Zilliacus Tommi Kekki



Why are we interested in Ruthenium

- During routine nuclear reactor operation, ruthenium will accumulate in the fuel in relatively high concentrations.
- In an accident in a nuclear power plant it is possible that air gets into contact with the reactor core. In this case ruthenium can oxidise and form volatile ruthenium species, RuO_3 and RuO_4 , which can occur in the containment
- The oxidation and release of Ruthenium can also be a problem in reprocessing of nuclear fuel



Objective of this study

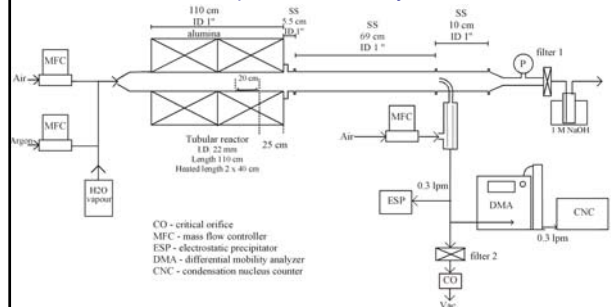
Study the effect of

- Oxygen partial pressure
- Oxidation temperature
- Tube material
- Seed particles
- Water vapour
- Gaseous RuO_4 injection ← studying at the moment

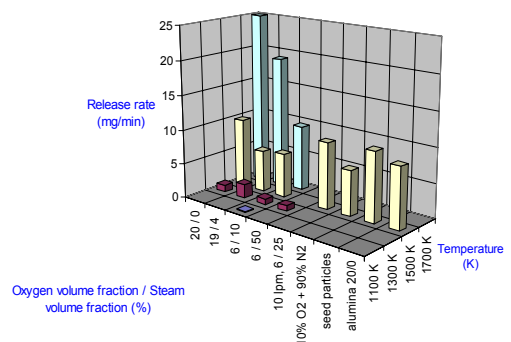
on ruthenium release, transport and speciation

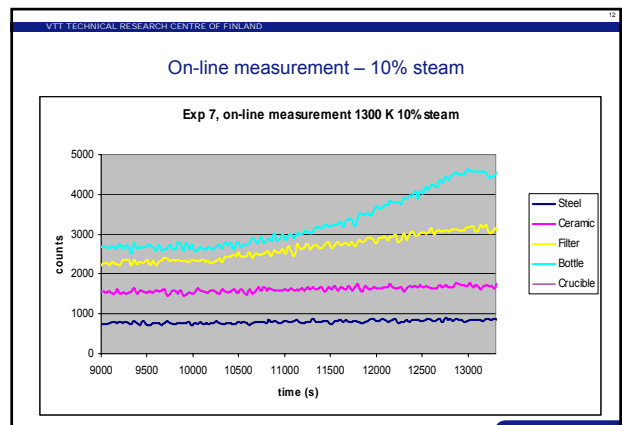
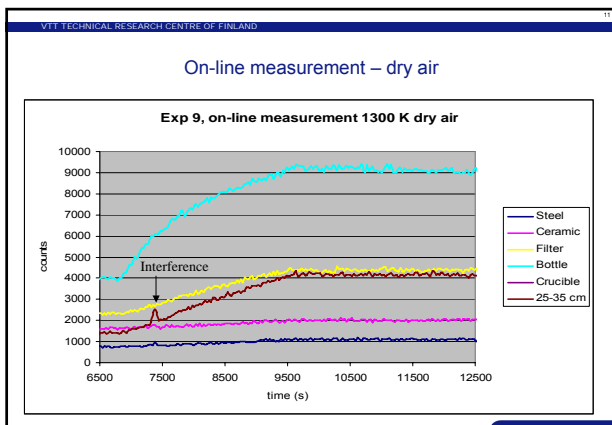
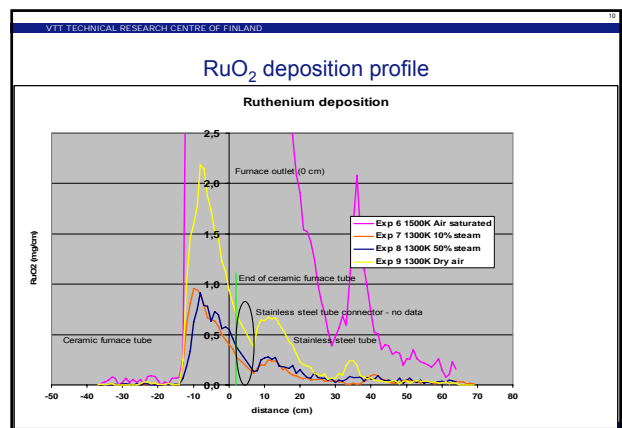
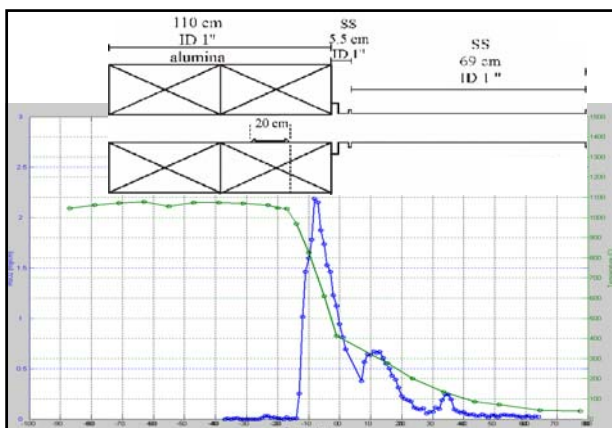
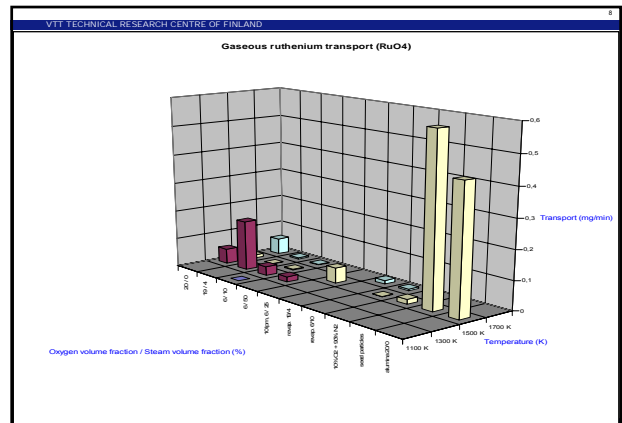
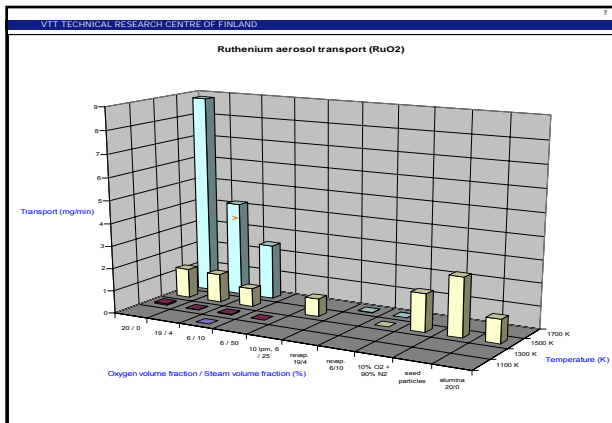


Experimental facility



Ruthenium release rate

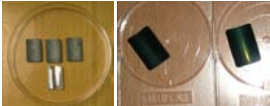




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Gaseous RuO₄ injection measurements

Exp #	T furnace [K]	Gas	Tube material	Duration [min]	Other
1.	1500	Saturated air + RuO ₄	Al ₂ O ₃	45	
2.	1500	Saturated air + RuO ₄	Al ₂ O ₃	45	γ-tracer
3.	1500	Saturated air + RuO ₄	SS	45	γ-tracer
4.	1500	Saturated air + RuO ₄	Al ₂ O ₃	45	γ-tracer SS-plates



Stainless steel plates

- non-oxidised
- oxidised
- non-oxidised + RuO₂ surface
- oxidised + RuO₂ surface

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Gaseous RuO₄ injection experiment 1

- Method to produce gaseous RuO₄
 - Reagents:
 - conc. sulfuric acid (H₂SO₄)
 - 0.3 M potassium permanganate (KMnO₄)
 - RuCl₃ dissolved in HCl (27.9 mg Ru/ ml)
 - 100 ml of concentrated H₂SO₄ is added to the distillation flask. The air inlet is connected and 5 ml of Ru-solution is added to the flask. The system is closed immediately. The flask is gently heated. The temperature in the gas outlet 20 cm above the flask rises from 23°C to 85°C. A drop of KMnO₄ solution from a dropping funnel is added to the H₂SO₄ – Ru -solution. The reaction is vigorous and brownish Ru gas can be seen flowing up. After some minutes another drop is added. This is repeated still 3 times.

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SS/ceramic tube

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Gaseous RuO₄ injection experiment 1

- Results
 - experiment was very difficult to control, because of vigorous formation of gaseous compounds while potassium permanganate (KMnO₄) was added
 - analysis of the samples was not a success due to low transport of ruthenium from distillation flask
 - next experiment with lower KMnO₄ concentration

Active gaseous RuO₄ injection experiment 2

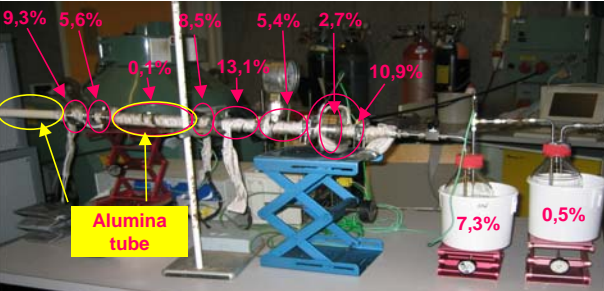
- Decreased concentration of KMnO₄: 0.03 M
 - less vigorous gas formation
 - γ-tracer enhances detection of ruthenium deposition

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Deposition of ruthenium in experiment 2

- Only few milligrams of ruthenium was transported from distillation flask and the duration of the experiment was 3,5 hours



Alumina tube

Deposition percentages (from left to right): 9,3%, 5,6%, 3,5%, 5,4%, 2,7%, 10,9%, 7,3%, 0,5%, 13,1%, 0,1%.

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Gaseous RuO₄ experiments 3 and 4

- Experiment 3: Preparation of Ru-solution in distillation flask in order to increase the amount of transported ruthenium during the experiment
 - > measure the amount of transported ruthenium through SS-tubing
- Experiment 4: Attach the already prepared SS-plates on ceramic tube surface
 - > measure the amount of deposited ruthenium on different steel surfaces

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Determination of granites mineral specific porosities by PMMA method and FESEM/EDAX

A Leskinen*, L Penttinen*, M Siitari-Kauppi*, U Alonso**, M Garcia-Gutierrez**, T Missana** and Alessandro Patelli***

*Laboratory of Radiochemistry, University of Helsinki, P.O. Box 55, FIN-00014 University of Helsinki, Finland

**Ciemat, Avda. Complutense 22 - 28040 Madrid, Spain

***CIVEN, Via delle Industrie 9, 30175 Venezia-Marghera, Italy

In the frame of geological disposal of nuclear fuel long lived radio nuclides or activation products may be released from the fuel to the geo/biosphere. In bedrock, contaminants will be transported along fractures by advection and retarded by sorption on mineral surfaces and by molecular diffusion into stagnant pore water in the matrix along a connected system of pores and micro fissures. Since chemical interactions of groundwater and transported components with inner mineral surfaces play a major role as retardation process, the effectiveness of the rock matrix as natural barrier is decisively influenced by size, shape and spatial arrangement of the effective rock porosity network. A reliable picture of the pore space structure in rock minerals phases can be achieved by using different complementary methods for characterisation.

The porosity of three granites; Grimsel granite (Switzerland), Ratones granite (Spain), El Berrocal granite (Spain) was studied by ^{14}C -polymethylmethacrylate method (^{14}C -PMMA) followed by field emission scanning electron microscope and electron dispersive roentgen spectroscopy (FESEM/EDS) analyses. The determination was focused on the mineral specific porosities because the uranium migration was investigated for the same sample types by two novel techniques; Rutherford backscattering spectrometry (RBS) and proton induced X-ray emission (μPIXE). The ^{14}C -PMMA method makes it possible to study the spatial distribution of the pore space and the heterogeneities of rock matrices on submicrometric to centimetric scales. Subsequent autoradiography and digital image analysis enable features limited in size by the range of ^{14}C beta radiation to be measured. The structures of various minerals were studied in more detail by using FESEM/EDS which allows the determination of minerals according to their elemental composition.

The total porosity of Grimsel granite (0.75%) was significantly higher than the porosities of Spanish granites (0.3%). The Grimsel granite feldspars porosities were twice to three times higher than the Spanish granites feldspars porosities however there was no significant difference between the dark minerals porosities. The clear difference was found between the various quartz grains. The Spanish granites quartz crystals were nonporous when measured by the PMMA method however the quartz of Grimsel granite showed 0.5% intra granular porosity. The Grimsel granite comes from young formation where the mineral crystallisation is ongoing process compared to the Spanish granites. It is interesting that different behaviour was observed amongst the obtained values. On one side, the apparent diffusion coefficients calculated for uranium diffusion within Grimsel granite on different minerals were very similar ($2 \cdot 10^{-13} \pm 0.5 \text{ m}^2/\text{s}$). On the other side, differences were found from one mineral to another ($9 \pm 1 \cdot 10^{-14} \text{ m}^2/\text{s}$ in feldspars and $4.5 \pm 0.5 \cdot 10^{-14} \text{ m}^2/\text{s}$ in quartz) on both Spanish granites, presenting always lower diffusion values than in the Grimsel granite. The differences in uranium migration is discussed on the grounds of porosity results.

Name	Anumaija Leskinen
Company / University	University of Helsinki
Web-page	www.helsinki.fi/kemia/radiokemia/
Phone (direct line)	+358 40-7231400
E-mail	anumaija.leskinen@helsinki.fi

DETERMINATION OF GRANITES' MINERAL SPECIFIC POROSITIES BY PMMA METHOD AND FESEM/EDAX

INTRODUCTION

The mineral specific porosities of three samples (El Berrocal, Grimsel and Palmottu) were determined by the ^{14}C -methylmethacrylate (^{14}C -PMMA) autoradiography method which offers to visualize the rock structures from micrometric to decimetric scales. Furthermore, scanning electron microscopy and energy-dispersive X-ray analysis (FESEM/EDAX) were performed in order to study the pore apertures of porous regions in greater detail and to identify the corresponding minerals. Some apparent diffusion coefficients for uranium are shown.

PMMA METHOD

- Centimetric scale rock sample
- Drying with heat in a vacuum chamber
- Impregnation with ^{14}C -labelled methylmetacrylate (MMA)
- Polymerization with irradiation
 - Heating at 120°C for 3 hours to release luminescence
- Slicing and polishing of inner surfaces with silicon carbide
- Exposure on autoradiographic film for 1-20 days
- Porosity calculations with Matlab program Mankeli; darker shades represent higher porosities



Figure 1. A vacuum chamber.

FESEM / EDAX

- Centimetric scale rock sample
- Polishing with diamond paste
- Carbon coating to prevent excitation
- Magnifications up to 1000 times with FESEM (Field Emission Scanning Electron Microscopy)
- Quantitative elemental analyses with EDAX (Energy Dispersive X-ray Analysis)



Figure 2. A SEM sample of the El Berrocal granite.

RESULTS AND CONCLUSIONS

The determined total porosities by the PMMA method for the El Berrocal granite is $0.45 \pm 0.05 \%$, for the Grimsel granodiorite is $0.79 \pm 0.05 \%$, and for the Palmottu granite is $0.64 \pm 0.05 \%$. The figures 3-11 present the autoradiographic, Mankeli, and SEM/EDAX images of the three samples.

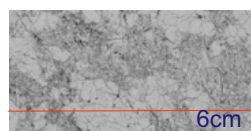


Figure 3. An autoradiographic image of the El Berrocal granite.

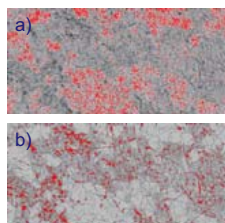


Figure 4a, b. A Mankeli images of the El Berrocal granite. The red areas represent porosities of under 0.1% (a) and over 1% (b).

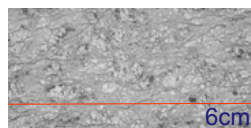


Figure 6. An autoradiographic image of the Grimsel granodiorite.

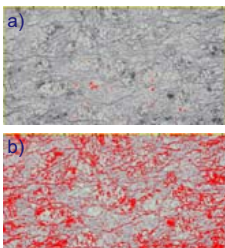


Figure 7a, b. A Mankeli images of the Grimsel granodiorite. The red areas represent porosities of under 0.1% (a) and over 1% (b).

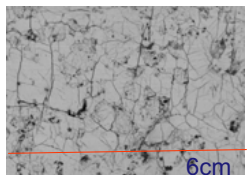


Figure 9. An autoradiographic image of the Palmottu granite.

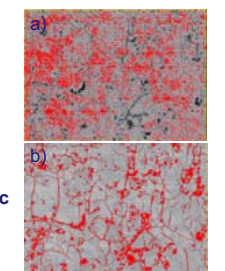


Figure 10a, b. A Mankeli images of the Palmottu granite. The red areas represent porosities of under 0.2% (a) and over 1% (b).

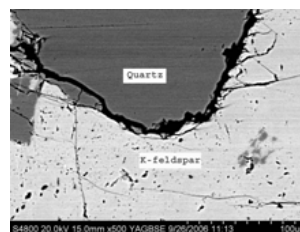


Figure 5. A SEM/EDAX image of the El Berrocal granite. The image is a 500 times magnification. The apparent diffusion coefficients for uranium by Rutherford Backscattering Spectrometry (RBS) are $9 \pm 1 \cdot 10^{-14} \text{ m}^2/\text{s}$ in feldspar and $4.5 \pm 0.5 \cdot 10^{-14} \text{ m}^2/\text{s}$ in quartz.

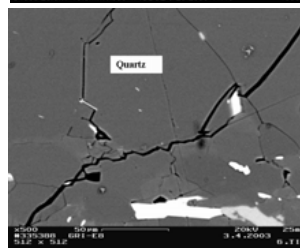


Figure 8. A SEM/EDAX image of the Grimsel granodiorite. The image is a 200 times magnification. The apparent diffusion coefficients for uranium by RBS on different minerals are very similar: $2 \cdot 10^{-13} \pm 0.5 \text{ m}^2/\text{s}$.

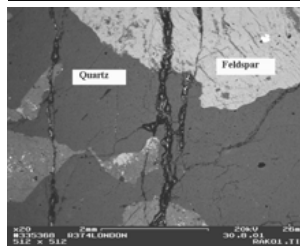


Figure 11. A SEM/EDAX image of the Palmottu granite. The image is a 20 times magnification and it shows a fissure aperture transecting quartz and feldspar grains.

A. Leskinen¹, L. Togneri¹, M. Siitari-Kauppi¹,
U. Alanso², M. Garcia-Gutierrez², T. Missana², A. Patelli³

1. Laboratory of Radiochemistry, University of Helsinki, P.O. Box 55, FIN-00014 University of Helsinki, Finland

2. Ciemat, Avda. Complutense 22 - 28040 Madrid, Spain

3. CIVEN, Via delle Industrie 9, 30175 Venezia-Marghera, Italy



Sorption of Cs to biotite

J. Kyllönen, M. Hakanen, A. Lindberg*

Laboratory of Radiochemistry, University of Helsinki, Al.Virtasenaukio 1, PL55, FI-00014 Helsingin yliopisto, Finland

*Geological Survey of Finland, Betonimiehenkuja 4, PL 96, FI-02151, Espoo, Finland

Biotite is the dominant mineral that sorbes Cs in granitic bedrock. Experiments were performed on biotites separated from drill core material from Olkiluoto site. The biotites were characterised for grain size, surface area (BET), element composition (EDX microanalyser) and mineral purity (XRD, point counting). Cation exchange capacities were determined using standard methods (AgTU, NH₄Ac) and sorption capacities for Ca, Na and Cs using radioactive tracers. The sorption processes of Cs was studied in simple electrolyte solutions and groundwater simulants. Experiments with simple electrolyte solutions and groundwater simulants were performed to determine the mass balance of Cs sorption. Selectivity coefficients of sorption were calculated. The minerals were examined with SEM after the sorption experiments, and with XRD for possible changes in the lattice where applicable. Phreeqc is used for mechanistic modeling of batch experiments in groundwater simulants and for simulating of flow experiments. The data from batch experiments is verified for flow conditions in crushed mineral column experiments and the need for scaling of sorption data to fracture flow conditions is studied.

Particle sizes of the biotites are < 0.5 mm and specific areas 0.6 to 0.8 m²/g. Mineral purity is > 90 %, the only major impurity is chlorite. Cation exchange capacities of the biotites are 0.013 meq/g to 0.018 meq/g. Cs sorption capacity in fresh groundwater simulant is equal to CEC, but in saline groundwaters the capacity is 1/3 of CEC. The major cation competing with Cs is K, but Na and Ca have to be taken account of when modeling the groundwater chemistry due to their high concentrations in the relevant groundwaters.

Name	Jarkko Kyllönen
Company / University	University of Helsinki
Web-page	www.helsinki.fi/kemia/radiokemia
Phone (direct line)	+358 9 191 50518
Fax	+358 9 191 50121
E-mail	jarkko.kyllonen@helsinki.fi

INTRODUCTION

Cesium sorption experiments were performed on biotite to determine the cation exchange properties of biotite and the selectivity coefficients of cation exchange for Na, K, Cs, and Ca.

SORPTION OF Cs TO BIOTITE

EXPERIMENTAL

The biotites were separated from drill core material from Olkiluoto site, characterised for grain size, surface area (BET), element composition (EDX micro analyser) and mineral purity (XRD, point counting). Unaltered biotite was used as a reference material. Cation exchange capacities were determined using AgTU and NH_4Ac standard methods.

The sorption process of Cs was studied in simple electrolyte solutions and groundwater simulants. Biotite was equilibrated in columns with suprapur quality reagents in order to occupy all cation exchange sites with Na, K or Ca. Cs sorption experiments were performed on these biotites in buffered solutions at pH 6 and 8 with ^{134}Cs -spiked solutions and non-spiked solutions. The sorption isotherms are in figures 1-3. The waters of the non-spiked experiments were analysed by ICP-MS.

The minerals are examined with SEM after the sorption experiments, and with XRD for possible changes in the lattice where applicable. Phreeqc is used for mechanistic modelling of batch experiments in groundwater simulants and for simulating of flow experiments. The data from batch experiments is verified for flow conditions in crushed mineral and fracture column experiments and the need for scaling of sorption data to fracture flow conditions is studied. Results from mica gneiss column experiments are in figure 4.

RESULTS

Particle size of the biotites is < 0.5 mm and specific areas vary from 0.56 to 0.83 m^2/g . Mineral purity is > 90 % for the Olkiluoto biotites, the only major impurity is chlorite. Cation exchange capacity of the biotites is 1.3 meq/100g to 1.8 meq/100g. Cs sorption capacity in fresh groundwater simulant is equal to CEC, but in saline groundwaters the capacity is $1/3$ of CEC. The major cation competing with Cs is K, but Na and Ca have to be taken account of when modelling the groundwater chemistry due to their high concentrations in the relevant groundwaters.

The work was financed by Posiva Oy and Ministry of Trade and Industry of Finland.

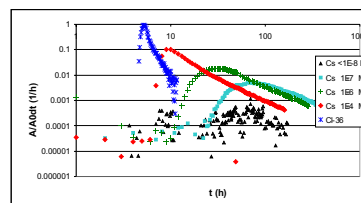


Figure 4. Breakthrough curves of pulse-injected ^{36}Cl and ^{137}Cs in mica gneiss columns. Flow rate is 0.9 ± 0.1 ml/min. Inventories are 100 % except for the $<1\text{E}-8$ M and $1\text{E}-7$ M concentrations, in which the inventories are 3 and 73 %, respectively.

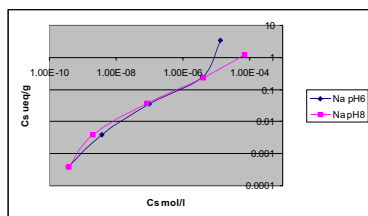


Figure 1. Sorption isotherm of Cs in 0.1 M NaCl

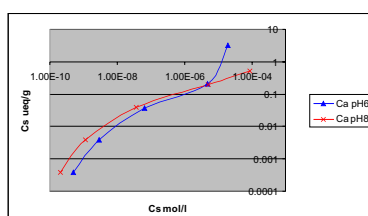


Figure 2. Sorption isotherm of Cs in 0.1 M CaCl_2

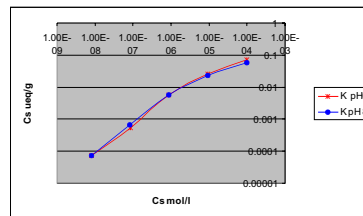


Figure 3. Sorption isotherm of Cs in 0.1 M KCl



Radioactivity distribution analysis with digital autoradiography at HYRL

L.Togneri, M.Siitari-Kauppi

Laboratory of Radiochemistry, P.O. Box 55, FIN-00014 University of Helsinki, Finland

Since the 1980's, film autoradiography (FA) has been used widely in nuclear waste management projects at HYRL for visualising radionuclide (RN) migration routes and sorption sites in crystalline granitic rock, as well as measuring the porosity and 2D pore structure in rocks. FA on x-ray films coated with AgBr grains has been the method of choice until now.

Polymethylmethacrylate (PMMA) porosity measurement method consists of ^{14}C or ^3H labeled organic solvent, methylemethacrylate (MMA), which is polymerized in rock matrix by ^{60}Co source to provide cm scale rock surfaces for FA. In FA the spatial resolution for low beta emitting RNs is high. However, the linearity of FA is poor due to the limited amount of AgBr grains on films. The highly advanced imaging methods, like digital autoradiography (DA) e.g. photosimulated luminescence (PSL) autoradiography are taking over, also in HYRL since 2004. The advantages of DA include a significantly better sensitivity and a linearity up to 105, which allows us to do exact quantitative analyses. The FLA scanner (FLA-5100, Fujifilm) is based on the use of a flexible Imaging Plate (IP), which is covered with small crystals of barium fluorobromide phosphor grains that contain a trace amount of bivalent europium as a luminescence center, and are stimulated by RN or visible light. Exposure of samples to the IP is performed in a manner similar to that of photo-film. The exposed IP is scanned with a laser beam of red light (635 nm). The PSL released upon the laser is collected into the photomultiplier tube (PMT) through the light collection guide and is converted to electric signals. The result is a 2D image showing the spatial distribution of RN in a sample. The exposed IP is reusable after erasing the residual latent image with uniformly irradiated visible light.

Applications for the FLA-5100 include:

- Characterisation of rock structures with the $^3\text{H}/^{14}\text{C}$ -PMMA-method.
- ^{18}F -compound purity measurements from TLC plates.
- Transport of ^{32}P and ^{45}Ca in a pea stem over time.
- Mineral sorption of ^{63}Ni , ^{134}Cs and ^{152}Eu on thin slices of different rock samples.
- Emittance measurements in the external beam line.
- Fluorescence detection (635nm) straight from the surface of samples doped with red colourant.

The resolution of pictures achieved depend strongly on the emitted β -energy; the lower the energy the better the resolution. The lowest pixel resolution achieved with the FLA scanner is 10 μm , when in x-ray films the resolution can be lower with low energy β -emitters.

^3H and ^{14}C standards from Amersham have been used to determine the accuracy and reproducibility of the specific activity analysis with the FLA scanner. The standards have been scanned with variable resolutions (10, 50 and 200 μm) after variable exposure times (from 8h to 7 days).

Name	Laura Togneri
Company / University	Laboratory of Radiochemistry, University of Helsinki, Finland
Web-page	http://www.helsinki.fi/kemia/radiokemia/
Phone (direct line)	+358919150519
Fax	+358919150121
E-mail	Laura.Togneri@helsinki.fi

RADIOACTIVITY DISTRIBUTION ANALYSIS WITH DIGITAL AUTORADIOGRAPHY AT HYRL

Abstract

Since the 1980s film autoradiography (FA) has been used widely in nuclear waste management projects for visualising radionuclide (RN) migration routes and sorption sites in crystalline granitic rock. FA on x-ray films coated with AgBr grains has been the method of choice until now. The highly advanced imaging methods, such as digital autoradiography (eg. photosimulated luminescence (PSL) autoradiography) are slowly taking over, and have also been used in HYRL since 2004.

FujiFilm FLA-5100

- § The new FLA-5100 imaging system allows imaging of fluorescent and radioisotopic samples.
- § The maximum area of scanning is 40 x 46 cm.
- § The lowest pixel size is 10 μm , but 50 μm pixel resolution is mainly used in analyses.
- § At HYRL the laser beam of red light (635 nm) is used on radioisotopic samples and to detect fluorescence.

Imaging Plates (IPs)

- § Imaging Plates are flexible image sensors in which bunches of very small crystals of photo-stimulable phosphor of barium fluorobromide containing a trace amount of bivalent europium as a luminescence center, formulated as BaFBr:Eu²⁺, are uniformly coated on a polyester support film.
- § Exposure of samples on IP is similar to photo-film.
- § The exposed IP is scanned with the 635 nm laser beam, the released photostimulated luminescence (PSL) is collected into the photomultiplier tube (PMT) and converted to electric signals.
- § Analysis of the picture data (.img or .tiff format) is done in the AIDA program.
- § The exposed IP is reusable after erasing the residual latent image with uniformly irradiated visible light.



Figure 1: FujiFilm FLA-5100 at HYRL

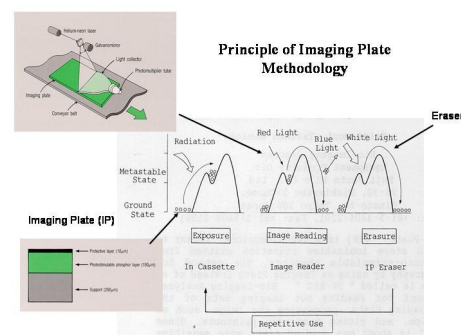


Figure 2: Principle of Imaging Plate Methodology

Digital autoradiography vs. film autoradiography

- § The area of linearity achieved with the FLA-5100 scanner is five orders of magnitude, when the linear area in film autoradiography is only two orders of magnitude (Figure 2).
- § The IPs are 50 – 100 times more sensitive than film autoradiography films. This allows shorter exposure times and a better separation power when using samples with high energy nuclides (Figure 4).
- § Film autoradiography gives better resolution for low beta energy nuclides, such as ³H.

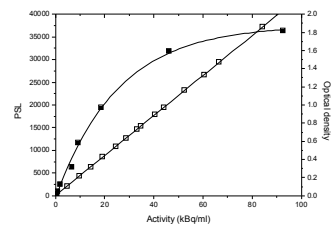


Figure 3: Linearity of a) film autoradiography (Kodak X-ray film, exposure time 7d, triangle) and b) phosphorimaging technique (Fuji Imaging Plate BAS-TR2025, exposure time 3d, square) determined for [¹⁴C]-PMMA standards.

Applications at HYRL

RADIOPHARMACEUTICAL RESEACRH

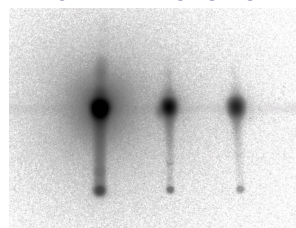


Figure 4:
Radiopharmaceutical compounds can be imaged with digital autoradiography with good separation power. E.g. ¹⁸F-compound on TLC-plate, exposed for 4 minutes.

FLUORESCENCE

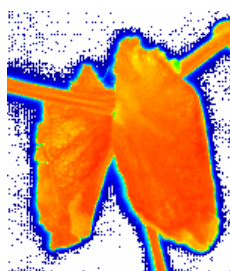


Figure 6:
The fluorescence detection is performed straight from the surface of the sample. E.g. after adding red colourant to a pea stem its veins can be imaged with great detail. This is part of a course work.

ROCK MATRIX CHARACTERISATION WORK

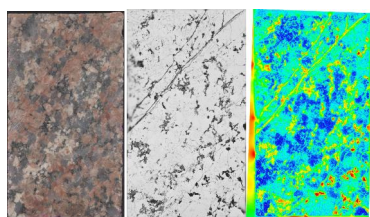


Figure 5:
Rock surface of granodiorite (left), film autoradiograph of 21d (middle) digital autoradiograph of 3d (right) achieved with ¹⁴C-PMMA method.

STANDARDISATION

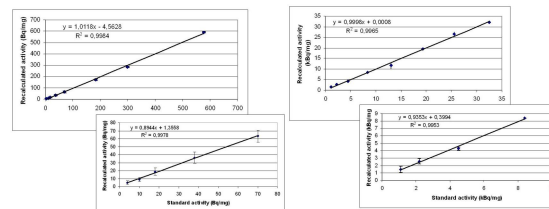


Figure 7: ³H standard

Figure 8: ¹⁴C standard

³H (3.7 – 577.2 Bq/mg) and ¹⁴C (1.1 – 32.5 kBq/mg) autoradiographic microscale standards from Amersham have been used to determine the accuracy and reproducibility of the specific activity analysis with the FLA scanner. The pixel resolution used was 200 μm and exposure times varied from 1 to 7 days. The average values of all analyses and their standard deviations are presented in the figures above. The low ³H and ¹⁴C activities cause some curvature in the standard lines' lower end. This is mainly caused by the need for long exposure times which leads to high background values.



Visualisation of conductive pore space by ^{14}C -PMMA impregnation

M. Kelokaski, M. Siitari-Kauppi, A. Möri*,
W. Kickmaier**, K-H. Hellmuth***

Laboratory of Radiochemistry, University of Helsinki, Finland

* University of Bern, Switzerland

** National Cooperative for the Disposal of Radioactive Waste, Wettingen, Switzerland

*** Finnish centre for Radiation and Nuclear safety, Helsinki, Finland

Due to uncertainties in transport pathway and real pore space characterisation, there has been a tendency to play down the potential role of the geosphere as a safety barrier in repository performance assessment. The repository safety evaluation today requires going from laboratory and surface-based field work underground to the repository level. For upscaling matrix diffusion and sorption processes to real in situ metre scale conditions we need realistic data of the physical rock matrix properties. Little is known about the changes of rock transport properties during sampling and decompression. Information on the reliability of laboratory-based rock characterisation methods by quantitative investigation on the effects of rock stress release on total and mineral-specific porosities is needed as a basis for the evaluation of changes in transport properties of different rock types under different stress conditions.

The ^{14}C -PMMA method has been developed for characterisation of pore space geometry for low permeability granitic rocks. Rock matrices have been studied so far at laboratory. The rock porosity, morphology of pore space i.e. tortuosity, constrictivity and pore apertures as well as the connectivity and accessible pore space from submicrometre to decimetre scales are studied. Impregnation with ^{14}C -labelled methylmethacrylate (^{14}C -MMA) and autoradiography allows the investigation of the spatial distribution of porosity. Quantitative measurement of total or mineral-specific, local porosities are also developed using image analysis tools.

The development of the ^{14}C -PMMA method for in situ application comprises impregnations of decimetre length rock cores, impregnations of rock blocks ($30 \times 30 \times 30 \text{ cm}^3$) in the laboratory, and furthermore, in situ impregnations conducted at the Grimsel Test Site within GTS Phase VI. The results of block scale investigations as well as the in situ experiment are reported here. In situ conditions were simulated at the block scale experiments by intruding ^{14}C -MMA into the water-saturated Kuru grey granite (permeability $10\text{--}18 \text{ m}^2$, porosity of 0.4%). Tests were focused on drying the matrix, impregnation in vacuum and optimising heating polymerisation conditions. Visualisation of conductive pore space was performed by autoradiography giving 2D images of intra- and intergranular pores of granite sample. Intragranular porosity could be revealed in these experiments in unsaturated zones implying that water effectively inhibits intrusion of ^{14}C -PMMA. In addition intrusion of ^{14}C -MMA into Grimsel granodiorite in situ was verified.

Name	Maarit Kelokaski
Company / University	University of Helsinki
Web-page	www.helsinki.fi/kemia/radiokemia
Phone (direct line)	+358 40 8699310
Fax	+358 9 19150120
E-mail	maarit.kelokaski@helsinki.fi

Abstract

The repository safety evaluation requires going from the laboratory underground, to the repository level. The ^{14}C -polymethylmethacrylate (PMMA) method has been developed for characterisation of the pore space geometry for low permeability crystalline rocks. The rock porosity, morphology of pore space and pore apertures, connectivity and accessible pore space from sub-micrometre to decimetre scales are studied. The development of the method for *in situ* application comprises impregnation of decimetre length rock cores and rock blocks in the laboratory and, furthermore, *in situ* impregnations conducted at the Grimsel Test Site (GTS), Switzerland.

Experimental conditions

Figure 1. Experiment setup for Kuru grey granite rock block. To simulate the *in situ* conditions, the rock block was placed in a water bath. An airtight casing prevented water loss during drying, impregnation and polymerisation.

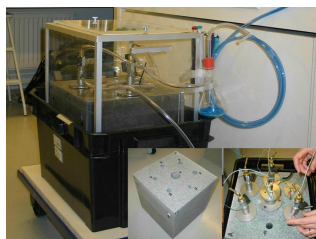
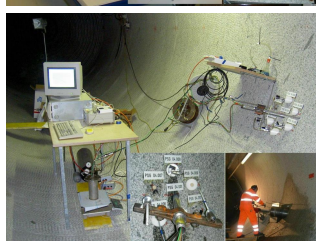


Figure 2. *In situ* experiment site located in the WT tunnel of the GTS. The length of the injection borehole was 1.27 m, diameter 4 cm. Overcoring was performed with a 300 mm single core barrel which provided an intact drillcore (PSG 04.001-OC) of 1.17 m length.



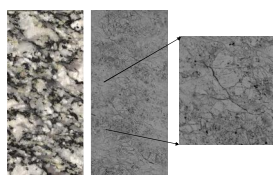
	core scale	block scale	<i>in situ</i>
rock matrix	Grimsel granodiorite,	Kuru grey granite	Grimsel granodiorite
dimensions	length 3 - 11 cm Ø 3 - 7 cm	30 cm × 30 cm × 30 cm	at the depth of 1 meter from the tunnel wall
drying	vacuum, aluminium chamber	air flushing + vacuum	air flushing
impregnation	vacuum, aluminium chamber	initial vacuum	5 bar pressure
polymerisation	irradiation with ^{60}Co source	heating, chemical initiator	heating, chemical initiator
tracer activity	888 kBq mL ⁻¹	888 kBq mL ⁻¹	22 kBq mL ⁻¹
analysis	* autoradiography (ag) * water and MMA gravimetry * PMMA and Hg porosimetry * SEM + CLSM	* autoradiography * water gravimetry * PMMA and Hg porosimetry	* water + thermo gravimetry * Hg porosimetry * CLSM * tracer activity too low for ag
depth of penetration	samples fully impregnated	max. 6 cm	max. 5 cm
porosity determined	0.75 ± 0.2 %	0.4 ± 0.1 %	from 0.5 to 0.1 %

scanning electron microscopy (SEM), confocal laser scanning microscopy (CLSM)

Experiment 1 – core scale

The pore space of different sized core samples could be completely impregnated under laboratory conditions once the sample was properly dried. Total porosities determined by the PMMA method (0.5 – 0.8 %) were in good agreement with porosity values measured with conventional methods (0.6 – 0.9 %). All mineral phases were found to be porous and could be visualised with PMMA autoradiographs (Figure 3). Inter- and intra-granular fissures and pore apertures in biotite and feldspar grains were visualised also by CLSM when ^{14}C -MMA was doped with fluorescein dye.

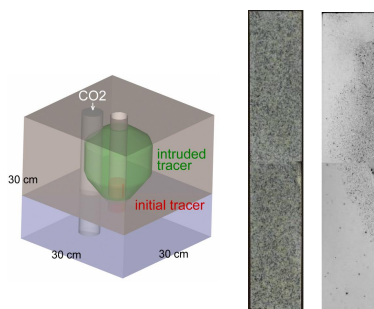
Figure 3. Scanned image of Grimsel granodiorite, corresponding autoradiograph (sample height 5 cm) and magnification showing the pore structure in detail (porosity 0.55%). Different shades of grey on the autoradiographs correspond to different porosities, the darker the shade, the higher the porosity.



Experiment 2 – block scale

^{14}C -MMA intruded to a maximum depth of 6 cm. Vacuum drying prior to impregnation clearly improved the penetration of the tracer. Porosity values (0.3 – 0.4 %) were congruent with results achieved in earlier lab experiments (0.4 %). The porosity (0.2 – 0.3 %) was slightly lower at the interface of ^{14}C -MMA and water. Grain boundary porosity dominated in that zone, otherwise intragranular pores were impregnated. The main reason for the insufficient intrusion of resin was found to be residual water in small pores.

Figure 4. Schematic diagram of the block scale experiment. The red area illustrates the location of resin in the injection hole, the green colour, the resin impregnated matrix. Six sub-samples (e.g. CO2) were cored and sawn into two pieces for autoradiography. Scanned image of Kuru grey granite sample and corresponding autoradiograph (sample height 28 cm, width 5 cm) on right hand side.



Experiment 3 – *in situ*

^{14}C -MMA intruded to a maximum depth of 5 cm into the rock matrix. Drying of rock around injection hole could have been more effective, but heating polymerisation of acrylic resin succeeded well. Several sub-samples of core slices were analysed with different porosimetry methods. Unfortunately, tracer activity was too low to obtain PMMA autoradiographs. Due to the shrinking of MMA, water saturation gravimetry showed 0.1% residual porosity for re-impregnated sub-samples taken from the overcore. Thermo-gravimetry (TG) porosity values (0.5 – 0.7%) were in good agreement with other results (0.5 – 1.0%). A borehole disturbed zone (BDZ) was found to exist in first three millimetres from the surface of the injection hole.

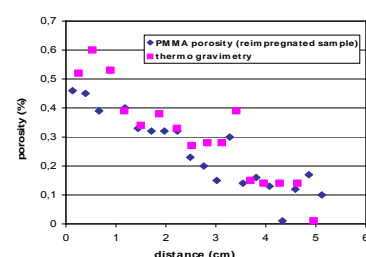
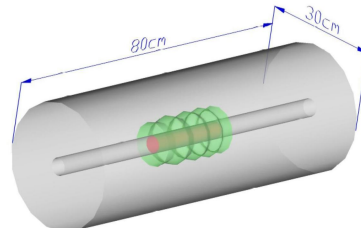


Figure 5. Schematic diagram of the *in situ* experiment. The red area illustrates the location of resin in the injection hole, the green colour, the resin impregnated matrix. Porosity values clearly decreased from the injection hole surface to a depth of 5 cm (measured by TG method and PMMA autoradiography after re-impregnation). Observations by CLSM were executed on the sub-samples from the core showing intrusion of MMA into all pore types and minerals apart from biotite phases.

Conclusions

Penetration of ^{14}C -MMA into Grimsel granodiorite *in situ* was successfully applied. Porosity values were 20-30% lower under *in situ* conditions than in the lab experiments, which is in agreement with earlier *in situ* experiments. However, in this *in situ* experiment insufficient intrusion of ^{14}C -MMA could have been caused by improper drying of open pore space. Water effectively inhibits intrusion in micro-pore apertures and therefore proper drying is required if the PMMA method is to be applied *in situ*.

SESSION II

Radiopharmacy and Dosimetry

Oral presentations

Anna Kirjavainen

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Semi Helin

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Stewart Makkonen-Craig

Recent Applications of Helsinki's Cyclotron

Poster presentations

Hanna Tuovinen, J. Lehto, Risto Paintner

A Case Study of Radiopharmaceutical Production ([¹⁸F]FDG) at the University of Helsinki

Tiina Lipponen, T. Koivula

¹⁸F-Radiochemistry in the University of Helsinki



[¹⁸F]fluoromethane as a precursor for ¹⁸F-labelling synthesis of radio- pharmaceuticals for Positron Emission Tomographic (PET) imaging studies

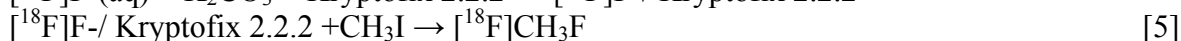
Kirjavainen A, Solin O

Radiopharmaceutical Chemistry Laboratory, Turku PET Centre, University of Turku, Turku, Finland

[¹⁸F]fluoromethane ([¹⁸F]CH₃F) is the simplest ¹⁸F-labelled organic molecule. It is used as a cerebral blood flow tracer in Positron Emission Tomography (PET) [1, 2]. Because fluoromethane is cleared rapidly by exhalation, its biological residence time is short. [¹⁸F]CH₃F allows repeat measurements in a single scanning session, while the relatively long physical half life of ¹⁸F allows multiple imaging studies with a single batch of tracers [3,4].

[¹⁸F]CH₃F is also used as the source of ¹⁸F-atoms in the isotopic exchange reaction in the production of ¹⁸F-labelled fluorine gas ([¹⁸F]F₂) with high specific radioactivity [5] [¹⁸F]F₂ is an important labelling precursor in the production of numerous important radiopharmaceuticals for PET (e.g. [¹⁸F]EF5 and [18F]FDOPA). The success and failure in the production of this labelling precursor is crucially dependent on the yield and quality of [¹⁸F]CH₃F.

Fluorine-18 (¹⁸F, β⁺, T_{1/2}=109.8 min) is produced by bombarding ¹⁸O-enriched H₂O with 18 MeV protons through the nuclear reaction ¹⁸O(p,n)¹⁸F. [¹⁸F]CH₃F is synthesized through nucleophilic displacement by a suitable leaving group from a methyl precursor. The nucleophilic fluoride reagent is generated from aqueous ¹⁸F-fluoride anion by azeotropic distillation and subsequent formation of an anhydrous cryptand complex:



Several radiochromatographic methods are used for purification and analysis of ¹⁸F-labelled compounds. RadioTLC is used for the analysis of possible residue of free ¹⁸F-fluoride. Labelled ¹⁸F-fluoromethane and derivatives are analyzed by radio-gaschromatography (radioGC).


Specific radioactivity is measured with GC/MS.

My Masters Thesis is on the synthesis of [¹⁸F]CH₃F from aqueous ¹⁸F-fluoride anion. The study includes testing several synthetic precursors (methyl halides, methyl triflate and possibly others), as well as identification of reaction products, and analysis of radiochemical yield and specific radioactivity of the product. Special attention is paid to high specific radioactivity and rapid chromatographic purification of this tracer.

References:

1. Gatley SJ, Hichwa RD, Shaughnessy WJ, Nickles RJ. Appl Radiat Isot 1981;32:211-4.
2. Wagner R. J Label Comp 1985;21:1229-30.
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5. Bergman J, Solin O. Nucl Med Biol 1997;24:677-83.

Name	Anna Kirjavainen
Company / University	University of Turku
Web-page	www.utu.fi
Phone (direct line)	+358 40 7775886
E-mail	akkirj@utu.fi




[¹⁸F]Fluoromethane as a precursor for ¹⁸F-labelling synthesis of radiopharmaceuticals for PET imaging studies

YoungRad seminar


14.12.2006 Anna Kirjavainen

Introduction




- The aim is to achieve production of [¹⁸F]F⁻ and [¹⁸F]CH₃F with the new cyclotron
- [¹⁸F]CH₃F is synthesized through nucleophilic displacement of a suitable leaving group from a methyl precursor
- Special attention is paid to high specific radioactivity and rapid chromatographic purification of this tracer

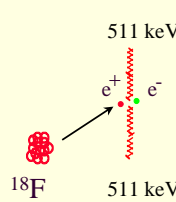
¹⁸F



- The half life of ¹⁸F is 109,8 min
- The nuclear decay involves 97% positron emission and 3% electron capture
- In the decay of ¹⁸F, 511 keV annihilation radiation is emitted


The decay of ¹⁸F



$$^{18}\text{F} \longrightarrow ^{18}\text{O} + e^+ + \nu$$



Solin 2004


Production of ¹⁸F-fluorine



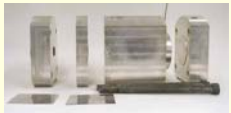

- ¹⁸F can be produced through several nuclear reactions:

- ¹⁸O(p,n)¹⁸F
- ²⁰Ne(d,α)¹⁸F
- ²³Na(³He,2α)¹⁸F
- ¹⁶O(³H,p)¹⁸F
- ¹⁹F(p,d)¹⁸F



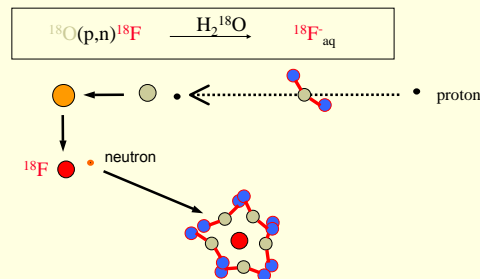


- Various target systems and target chamber materials, such as Al, Ni, Ag, Nb, Ti, Au, can be used

Production of ^{18}F -fluoride in Turku

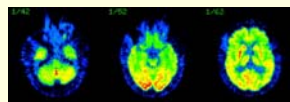
- In Turku, ^{18}F -fluoride is produced through the $^{18}\text{O}(\text{p},\text{n})^{18}\text{F}$ nuclear reaction
- ^{18}O -enriched water is irradiated with 18 MeV protons
- New cyclotron CC-18/9



Solin 2004

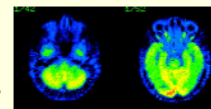
$[^{18}\text{F}]\text{CH}_3\text{F}$

- $[^{18}\text{F}]\text{CH}_3\text{F}$ is an important source of ^{18}F -atoms in the production of $[^{18}\text{F}]\text{F}_2$
- $[^{18}\text{F}]\text{F}_2$ is used in several synthesis of radiopharmaceuticals for PET (e.g. $[^{18}\text{F}]\text{EF5}$ and $[^{18}\text{F}]\text{FDOPA}$)
- $[^{18}\text{F}]\text{CH}_3\text{F}$ is used as a cerebral blood flow tracer for PET
- The low positron energy of ^{18}F -fluorine gives PET images of excellent resolutions



Physiological properties of $[^{18}\text{F}]\text{CH}_3\text{F}$

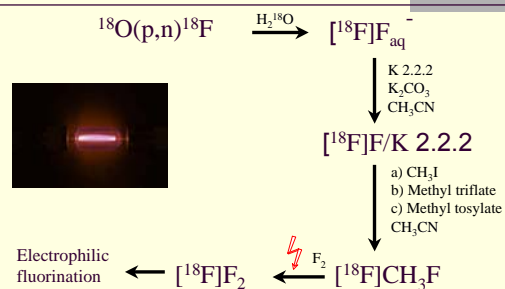
- $[^{18}\text{F}]\text{CH}_3\text{F}$ is metabolically inert in the human body
- $[^{18}\text{F}]\text{CH}_3\text{F}$ is gas at room temperature, and it is cleared by exhalation
- The relatively long physical half life of ^{18}F allows multiple imaging studies with a single batch of tracer
- Its biological residence time is short, which allows repeat PET-measurements in a single scanning session



Specific radioactivity

- High specific radioactivity is one of the most important qualities of a tracer, in addition to chemical and radiochemical purity
- When the specific radioactivity is high, the mass of radiotracer dosed is small
- Specific radioactivity declines with the physical half- life of the radioisotope.

Synthesis of $[^{18}\text{F}]\text{CH}_3\text{F}$



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Hot cell



- 16 hot cells in two laboratories in Turku PET-Centre

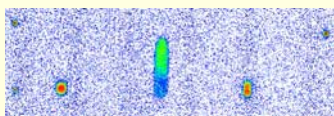
Synthesis apparatus



Analysis methods



- RadioTLC



- RadioGC

- GC/MS/MS



Conclusions



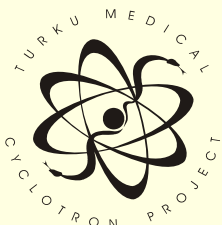
- The actual synthesis development is at an early stage, and therefore the analysis methods have not been thoroughly tested
- The success and failure of the production of $[^{18}\text{F}]\text{F}_2$ is crucially dependent on the yield and quality of $[^{18}\text{F}]\text{CH}_3\text{F}$

Many thanks to:

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Non-targeted effects of ionising radiation - bystander effect and genomic instability

Heli Mononen, Marjo Perälä, Oleg V. Belyakov
STUK-Radiation and Nuclear Safety Authority

Traditionally it is thought that biological effects of radiation result from direct DNA damage that occurs during or very shortly after irradiation of the nuclei in targeted cells. A range of evidence has emerged that challenges the classical effects resulting from targeted damage to DNA. Bystander effect and genomic instability are both considered as non-targeted effects of ionising radiation. An essential feature of these non-targeted effects is that they do not require a direct nuclear exposure by irradiation to be expressed and they are particularly significant at low doses. Recent studies suggest that bystander effect and genomic instability are interrelated.

We have studied bystander effect and genomic instability in telomerase immortalised normal human cells and 3D in vivo like human skin tissue systems after conventional and microbeam irradiation and based on the experimental data we have been able to demonstrate a clear bystander decrease in clonogenic survival, increase in micronucleation and apoptosis for both cell and tissue systems.

The new four-year European Integrated Project NOTE (Non-targeted effects of ionising radiation), which is coordinated by STUK - Radiation and Nuclear Safety Authority, was launched in September 2006. The focus of the project is on investigating the mechanisms underlying non-targeted effects. Another aim is to study if non-targeted effects modulate health risk at low doses and if ionising radiation can induce non-cancer diseases.

Name	Heli Mononen
Company / University	STUK-Radiation and Nuclear Safety Authority
Web-page	www.stuk.fi
Phone (direct line)	+358 9 759 88 551
Fax	+358 9 759 88 464
E-mail	heli.mononen@stuk.fi

Non-targeted effects of ionising radiation - bystander effect and genomic instability

Heli Mononen

YoungRad Seminar, 14-15 December Hotel Arthur, Helsinki, Finland



STUK-Radiation and Nuclear Safety Authority

Research and Environmental Surveillance, Radiation Biology Laboratory



14.12.2006

heli.mononen@stuk.fi

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Aims

- Study mechanisms of bystander effects after microbeam irradiation in 3D *in vivo* like human skin tissue models and eventually in primary human skin explants
- Develop methods of low dose irradiations of 3D tissue models with microbeam irradiation facilities
- Identify mechanisms and biological meaning of bystander effect in 3D tissue conditions

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heli.mononen@stuk.fi

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Materials

- Cell lines:
 - infinity telomerase-immortalised cell lines: human fibroblasts (hTERT-BJ1) and epithelial (hTERT-RPE1)
- MatTek artificial 3D *in vivo* like human skin tissues
- Primary human skin explants

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heli.mononen@stuk.fi

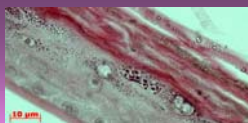
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MatTek artificial 3D *in vivo* like human skin tissue

- Experimental models - tissue-like intercellular cell signalling and 3D structure
- Artificial tissue model closely resembles epidermis of normal human skin

We are currently using two different models:

- differentiated EPI-200 (10-12 cell layers, ~75-100 µm thick) and
- underdeveloped EPI-201 (3-5 cell layers, ~20-45 µm).



EPI-200-33A - 5 µm paraffin section with haematoxylin-eosin staining.

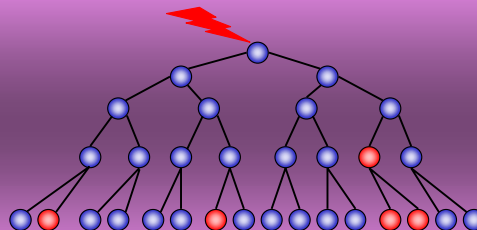
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Genomic instability

Irradiation



Radiation-induced genomic instability is defined as a persistent elevation in the rate of *de novo* appearance of genetic changes within a clonal population.

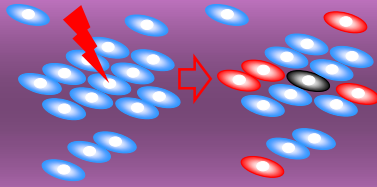
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Radiation induced bystander effect

Irradiation



- Directly hit cell marked black, bystander cells presented red (Belyakov *et al.* 2001a).

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heli.mononen@stuk.fi

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Exposure to ionising radiation

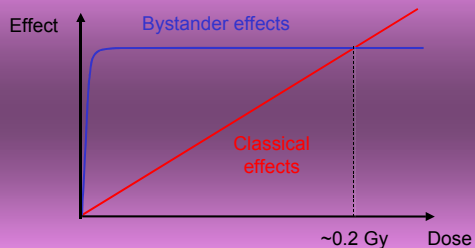
- Exposure to broad field X-rays
- Partially shielded X-ray exposure
- Medium transfer technique
- Microbeam irradiation with α -particles and protons

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heli.mononen@stuk.fi

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Contribution of bystander and direct components to the radiation induced damage



Comparison of the shapes of dose response curves of classical and bystander effect (Belyakov *et al.*, 2001a)

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heli.mononen@stuk.fi

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Mechanism of bystander effect

- Mechanism is not clear
 - two possible pathways:
 - by soluble cell culture medium mediated factor
 - through gap junctions

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heli.mononen@stuk.fi

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Methods to study bystander effect

- medium transfer
- partially shielded cell cultures
- charged particle microbeam irradiations (single spot)

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heli.mononen@stuk.fi

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Endpoints

- A range of different endpoints are used for studying the bystander effect and genomic instability in fibroblast, epithelial cells and artificial tissues
 - cell survival assay
 - micronucleus assay & total cellular damage
 - 3'-OH DNA end-labelling technique

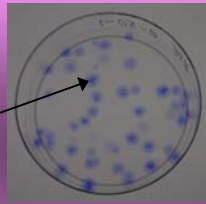
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heli.mononen@stuk.fi

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Cell survival assay

Clonogenic cell survival assay (Puck&Markus Technique)
• colonies with >50 cells were scored
-> representing cells with clonogenic potential



Epithelial cells plated on a 100mm diameter cell culture dish, irradiated with different doses and 14 days after plating removed from the incubator, fixed and stained (0,2% methylene blue in 70% ethanol).

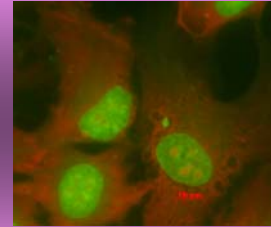
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Micronucleus assay

- Micronuclei are formed by lagging chromosomes or chromosomal fragments, which are not included in the nuclei during anaphase in cell division (Countryman and Heddle, 1976).



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heli.mononen@stuk.fi

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Total cellular damage

Total cellular damage (TCD) assay is a combination of micronucleus test and scoring of apoptosis according to morphological criteria (Abend, *et al.*, *IJRB*, 1995, 1996, 2000) .

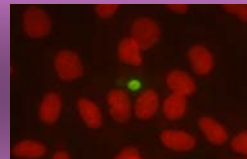
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heli.mononen@stuk.fi

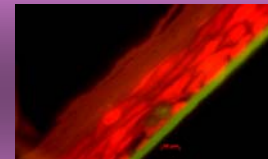
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3'-OH DNA end-labelling technique

Biochemically attributed apoptosis was assessed *in situ* with 3'-OH DNA end-labelling using the ApopTag Plus Fluorescein *In Situ* Apoptosis Detection Kit (Chemicon Int., USA)



RPE1 cells fixed with 1% paraformaldehyde and stained with ApopTag. Apoptotic bright green cellular nuclei.



Epi200, 5 µm paraffin section (63xobj.). Bystander apoptotic cells are green (Zeiss Axiomager). Sample was irradiated to a single position ($\pm 2 \mu\text{m}$).

14.12.2006

heli.mononen@stuk.fi

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Future...

14.12.2006

heli.mononen@stuk.fi

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NOTE

(Non-targeted effects of ionising radiation)

- September 2006 - August 2010
- Aims to expand the current understanding of health effects caused by low-level doses of ionising radiation
- **Key focus** of the research programme:
 - possible health consequences of exposures to small radiation doses which have not been investigated sufficiently so far
- **Objectives:**
 - to investigate the mechanisms underlying non-targeted effects
 - to investigate if non-targeted effects modulate health risk at low doses and if ionising radiation can induce non-cancer diseases
- **Website:** <http://www.note-ip.org>

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heli.mononen@stuk.fi

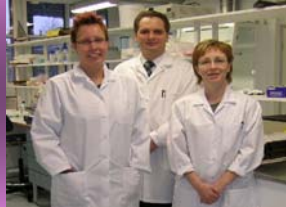
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NTIRE Non-Targeted
Ionizing Radiation Effects
Research Group

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heli.mononen@stuk.fi

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EPR dosimetry using lithium formate for measurements in narrow radiation fields

H. Gustafsson*, S. Olsson[#] och E. Lund*

* Department of Medicine and Care, Radiation Physics, Faculty of Health Sciences, University of Linköping, S-581 85 Linköping, Sweden

[#] Division of Radiation Physics, Linköping University Hospital, S-581 85 Linköping, Sweden

In intensity modulated radiation therapy, IMRT, the photon beam may be shaped by a multi leaf collimator to the shape of the target volume¹. In some directions the fields may be narrow and due to lack of electron equilibrium² the calculated dose distributions will be uncertain. For this reason an experimental verification of the calculated dose distributions is needed before treatment. Due to small geometries and high doses, even experimental determinations of absorbed doses could be a complicated task.

EPR-dosimetry has several advantages over current methods for measurements of absorbed dose in narrow beams. EPR-dosimeters can be made sufficiently small and they have a linear dose response over a broad dose range. Further, many materials for EPR-dosimetry are water and tissue equivalent, which is important for an accurate determination of absorbed dose when the energy spectrum is not completely known (inside a phantom for instance). Even though it has been found that EPR dosimetry using the amino acid alanine as dosimeter material may be used for accurate measurements of higher doses, EPR dosimetry using alanine as dosimeter material suffers from the drawback of a low signal to noise ratio at low doses. It has therefore been hard, on a routine basis, to measure clinical relevant doses with the precision demanded by ICRU.

Great effort has been paid to identify new materials suitable for EPR-dosimetry at low doses [3,4]. Among the candidates, lithium formate has properties that are especially good for EPR-dosimetry [5,6,7]. The increased signal to noise ratio compared to alanine offers a possibility to measure doses in the order of 1 Gy with the precision stated by the ICRU.

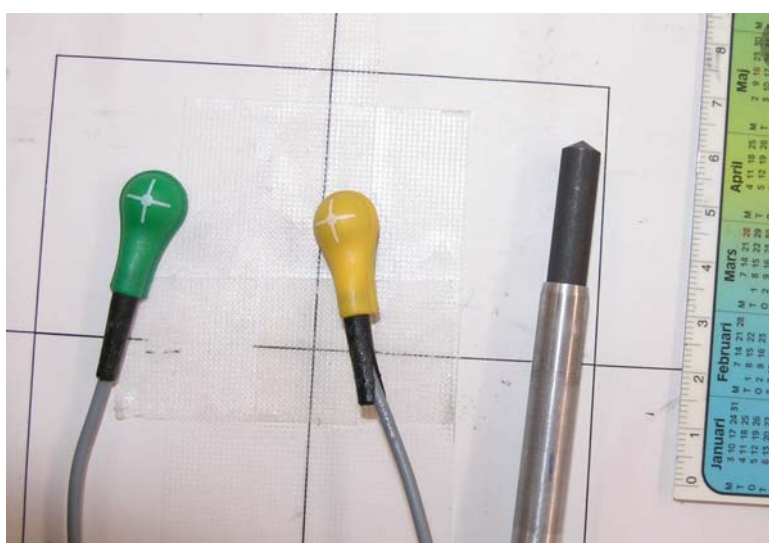
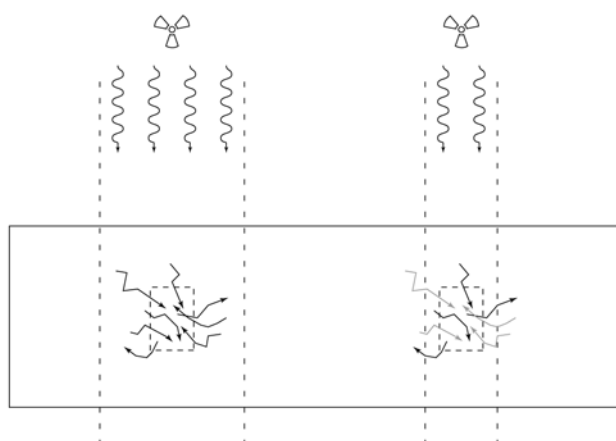
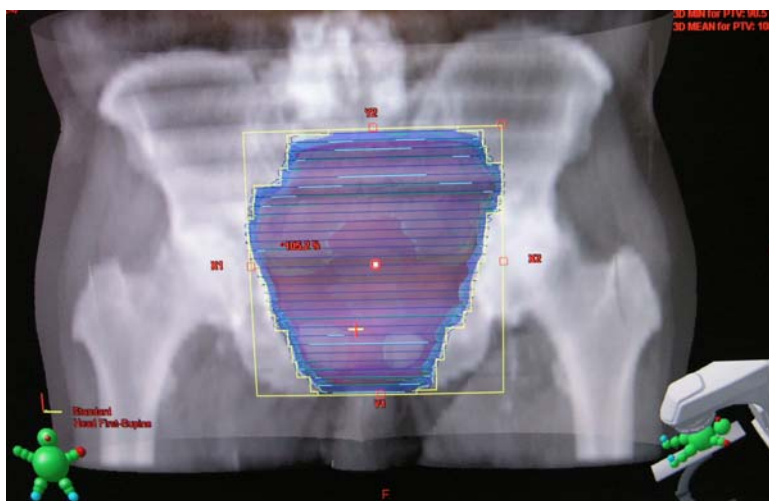
We have developed a protocol for determinations of absorbed doses in water in order to study the precision and accuracy of lithium formate dosimeters. The investigation shows that it is possible to measure doses with one standard deviation of less than 50 mGy. We can therefore determine a dose of 2 Gy in water with an accuracy of 5% (two standard deviations). Thus EPR-dosimetry using lithium formate dosimeters are an alternative for dose determinations in narrow radiation fields, especially if we can reach a precision better than 50 mGy.

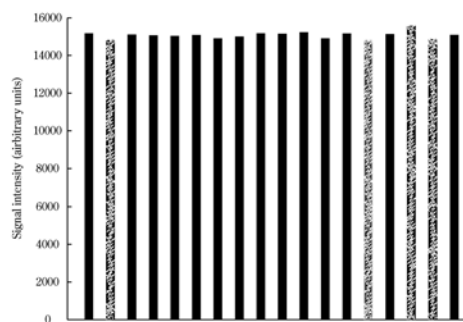
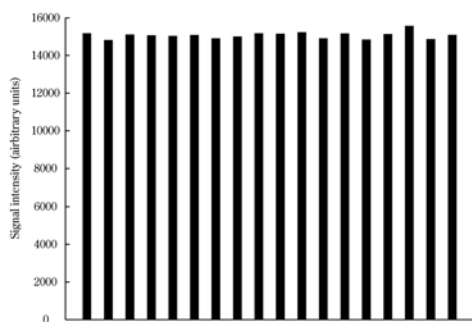
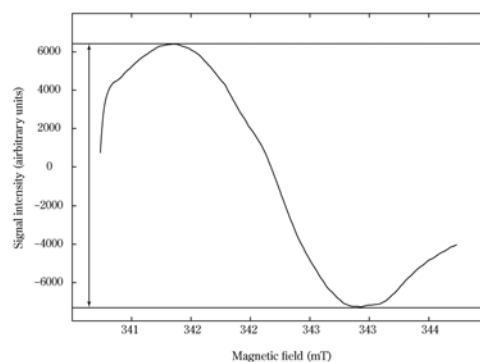
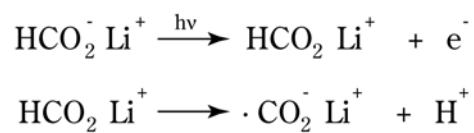
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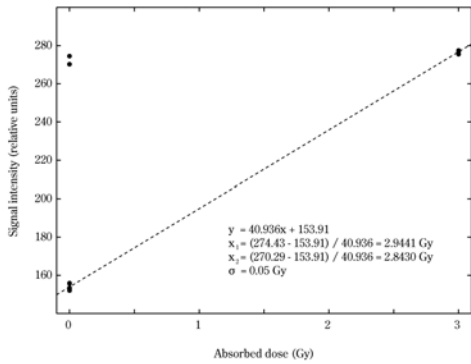
Name	Håkan Gustafsson
Company / University	Linköping University, Sweden
Web-page	http://huweb.hu.liu.se/inst/imv/radiophysik/forsk/index.html
Phone (direct line)	+46 13 223452
E-mail	hakgu@imv.liu.se

EPR dosimetry using lithium formate for measurements in narrow radiation fields

Håkan Gustafsson
IMV/Radiation Physics
Linköping University







Measured dose	Given dose	Error
2.94 Gy	2.912 Gy (IMRT-plan)	+ 28 mGy
2.84 Gy	2.826 Gy (IMRT-plan)	+ 14 mGy
1.73 Gy	1.80 Gy	- 70 mGy
0.59 Gy	0.60 Gy	- 10 mGy
0.24 Gy	0.20 Gy	+ 40 mGy
1.236 Gy	1.200 Gy	+ 36 mGy
3.452 Gy	3.500 Gy	- 48 mGy
0.268 Gy	0.300 Gy	- 32 mGy

An unknown dose can be measured in the interval
0 - 10 Gy, with one standard deviation of less than 50 mGy.

The uncertainty is less than 100 mGy using a 95 % confidence interval.

For a dose of 2 Gy or more, the uncertainty is less than 5 % of the dose.

In the future...

$2 \sigma < 98 \text{ mGy}$

Faster measurements of unknown doses.



[¹⁸F]FDG and its radioactive metabolites in biological samples

Rokka J, Haaparanta-Solin M, Solin O.

Turku PET Centre and Department of Chemistry, University of Turku, Turku, Finland

2-[¹⁸F]Fluoro-2-deoxyglucose ([¹⁸F]FDG) is a widely used radiopharmaceutical in clinical and scientific positron emission tomography (PET) studies to assess glucose utilisation in tissue. These measurements are originally developed to measure local cerebral glucose utilisation rates. [¹⁸F]FDG is converted to 2-[¹⁸F]fluoro-2-deoxyglucose-6-phosphate ([¹⁸F]FDG-6-P) and is trapped inside the cell. However, many researches have shown that in several tissues there is also [¹⁸F]FDG-metabolism beyond [¹⁸F]FDG-6-P [1,2].

In this study radioactive metabolites of [¹⁸F]FDG were prepared in vitro and sensitive radiochromatographic methods were developed for the analysis of [¹⁸F]FDG and its metabolic products from biological samples.

[¹⁸F]FDG was synthesized at the Turku PET Centre by a nucleophilic method modified from the synthesis of Hamacher et al. [3]. Enzymes used in the synthesis of FDG metabolites were all commercially available and syntheses were done using standard enzymatic methods [4]. The enzymatically produced FDG metabolites were used as standards when radiochromatographic methods were developed. ¹⁸F-Radioactivity (¹⁸F, β⁺, T_{1/2}=109.8 min) was analysed either by digital autoradiography for TLC-plates or by a pair of on-line-scintillation detectors in coincidence for annihilation radiation at the outflow of HPLC-columns.


Three different [¹⁸F]FDG metabolites, [¹⁸F]FDG-6-P, [¹⁸F]FDG-1,6-P2 and [¹⁸F]FD-PGL were prepared in vitro and several radioTLC and radioHPLC methods were tested for the metabolite analysis. Both radioanalytical methods have their own advantages. The radioTLC methods are useful when sample quantities are small and the amount of radioactivity is low, chemical resolution is however better in radioHPLC methods.

The methods developed can then be used for analyses of [¹⁸F]FDG metabolites from animal tissue samples when the metabolic profile of [¹⁸F]FDG is of interest.

Reference:


- [1] Suolinna E-M, Haaparanta M, Paul R, Härkönen P, Solin O, Sipilä H. Nucl Med Biol 1986;13:577–81.
- [2] Kaarstad K, Bender D, Bentzen L, Munk O L, Keiding S. J Nucl Med 2002;43:940–7.
- [3] Hamacher K, Coenen HH, Stöcklin G. J Nucl Med 1986;27:235–8.
- [4] Bergmeyer HU. Methods of Enzymatic Analysis, 3rd Edition, 1974, Weinheim Verl. Chemie.
- [5] Johanna Rokka, Masters Thesis 2006, Department of Chemistry, University of Turku, Turku, Finland

Name	Johanna Rokka
Company / University	Turku PET Centre, University of Turku
Web-page	http://pet.utu.fi/
Phone (direct line)	+358 50 5288408, +358 2 3337020
Fax	+358 2 3337000
E-mail	johanna.rokka@utu.fi

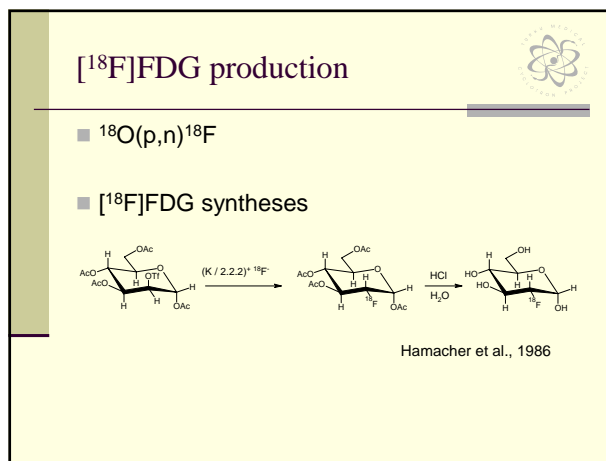
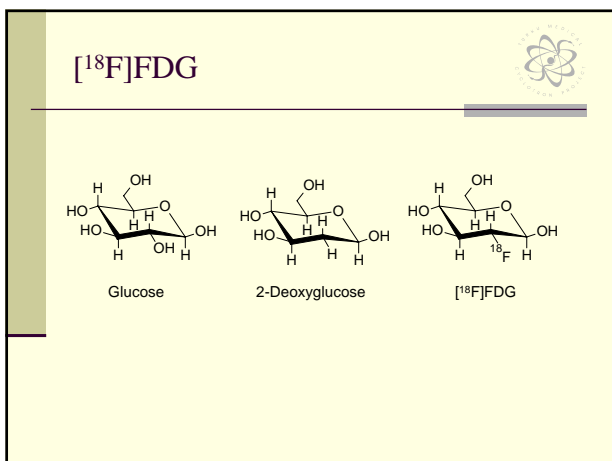
 **[¹⁸F]FDG and its radioactive metabolites in biological samples**


YoungRad seminar

14.12.2006 Johanna Rokka

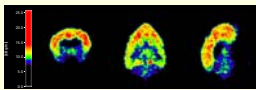
Turku PET Centre 


- A national Research Institute for Positron Emission Tomography, PET
- owned by University of Turku, Åbo Akademi University and Turku University Hospital
- about 120 persons in staff and investigators
- 4 PET-scanners
- > 30 PET-tracers in routine use
- www.turkupetcentre.fi

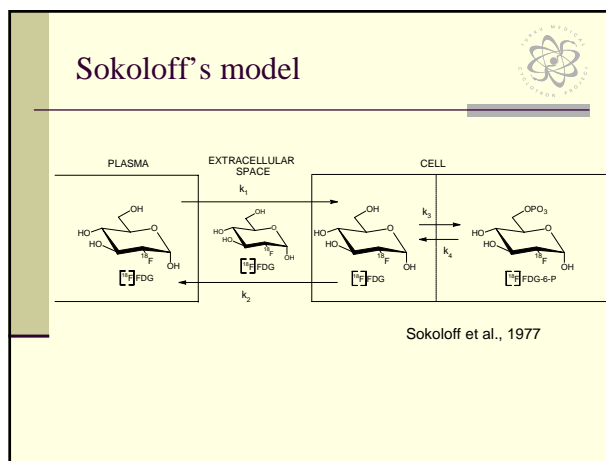


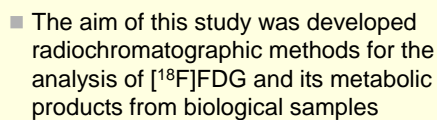
[¹⁸F]FDG & PET 

O[C@H]1O[C@H](O)[C@H](O)[C@@H](O)[C@H]1F

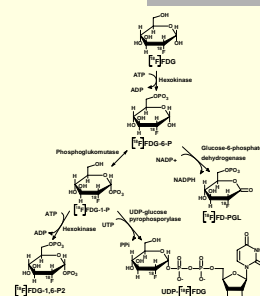








- Enzymatic reactions were used to make [^{18}F]FDG's metabolites in vitro
- Metabolites were used as standards when radiochromatographic methods were developed



- Several radioTLC methods were tested
- Radioactivity was detected using digital autoradiography



- Merck Hitachi's HPLC-system LaChrom L-7000
- Radioactivity was detected with a pair of NaI(Tl) scintillation detectors in coincidence



- Permission for the use of test animals for this study was obtained from the Ethnical Committee for Experimental Animals at the University of Turku
- The tissue metabolic profiles of [^{18}F]FDG was determined using radiochromatographic methods

- Two radiochromatographic method were developed to analyze metabolites of [^{18}F]FDG
 - RadioTLC is highly sensitive
 - RadioHPLC has very good chemical resolution
- Biological samples metabolic profile of [^{18}F]FDG can be determined using these radiochromatographic methods



Production of high specific radioactivity radiopharmaceuticals from [^{11}C]methane

Semi Helin, Eveliina Arponen, Kjell Någren

Radiopharmaceutical Chemistry Laboratory, Turku PET Centre, PO Box 52, FIN-20521 Turku, FINLAND.

PET imaging using radiopharmaceuticals is based on the tracer principle and thus is regarded as a non-invasive technique. The concept requires that the amount of the used radiopharmaceutical is at such a low scale that the examined biosystem is not altered nor experiences any physiological effect. To fulfil these requirements high specific radioactivity (SRA) is needed, meaning the amount of stable compound is low. Especially PET studies of low concentration receptor populations necessitate use of high SRA radiopharmaceuticals in order to prevent substantial (>5%) receptor occupancy. Also very potent compounds can be used if the injected mass is less than the defined limit for physiological effects.

In Turku PET Centre the systems used to produce the labelling reagent, [^{11}C]methyl triflate via [^{11}C]methyl iodide, are based on either in-target produced [^{11}C]CO₂ or [^{11}C]CH₄. The [^{11}C]CO₂ wet method utilising LiAlH₄, THF and HI is vulnerable in respect of high SRA and cumbersome due to using harsh reagents, which contain, absorb (from air) and produce carrier carbon [1] [2]. The struggle against dilution by atmospheric CO₂ and reagent origin carrier has been encountered with the gas-phase iodination method for the conversion of [^{11}C]methane to [^{11}C]methyl iodide. The original commercial system used [^{11}C]methane that was prepared from target produced [^{11}C]carbon dioxide and recirculation approach [3]. Recently, a single pass production of [^{11}C]methyl iodide from in-target produced [^{11}C]methane with improved specific radioactivity has been reported [4]. This improvement of SRA was due to the in situ production of [^{11}C]methane, the use of a single pass method, or a combination of both. In order to minimise carrier carbon sources attention has also been paid to the target construction [5].

Aiming to improve the SRA of the [^{11}C]radiopharmaceuticals we have constructed a system for the conversion of [^{11}C]methane to [^{11}C]methyl iodide which combines the recirculation setup, in situ production of [^{11}C]CH₄ and the special target modifications.


As a result, significantly improved SRA for ^{11}C -radiopharmaceuticals is achieved; values are over ten times higher compared to the [^{11}C]CO₂ system. In the system usage history a recurrent trend is observed where the SRA improves markedly in successive runs and usually goes down after maintenance or stand-by period.

In conclusion, the [^{11}C]CH₄ system has demonstrated capability for routine production of [^{11}C]radiopharmaceuticals with high specific radioactivity enabling PET studies without significant receptor occupancy or physiological effects. Further, the SRA levels are higher than typically obtained with another widely used labelling isotope, fluorine-18, thus promoting carbon-11 for PET studies when high SRA is demanded.

References

- [1] Iwata R, Ido T, Ujiie A, et al., Appl Radiat Isot, 39, 1-7, (1988)
- [2] Harada N and Hayashi N, Appl Radiat Isot, 44, 629-630, (1993)
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- [4] Zhang M-R, Haradahira T, et al., Nucl Med Biol 29, 233-241, (2002)
- [5] Björk H, Dahlström K, et al., Production of in-target ^{11}C CH₄ on a specific activity optimized ^{11}C PETtrace target, 10th Workshop on Targery and Target Chemistry, Madison (2004).

Name	Semi Helin
Company / University	Turku PET Centre / Turku University
Web-page	http://www.turkupetcentre.fi/
Phone (direct line)	+358 2 2154913
Fax	+358 2 3336255
E-mail	semi.helin@abo.fi



Production of High Specific Radioactivity Radiopharmaceuticals from $[^{11}\text{C}]\text{Methane}$


YoungRad-seminar
December 2006, Helsinki

14.12.2006

Turku PET Centre

Semi Helin

Outline




- Background
 - Radiochemistry at Turku PET Centre
 - Specific radioactivity
 - Need of high specific radioactivity
- Aims
 - Evaluate the new production method and the effect of the target modification
- Experimental part
 - Modified target & $[^{11}\text{C}]\text{CH}_3\text{I}$ production system
- Results
- Conclusions


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Background – Where I come




- Turku PET Centre
 - University of Turku
 - Åbo Akademi
 - Turku University Central Hospital
- Facility
 - Radiochemistry laboratory
 - Located in 2 buildings
- 3 cyclotrons
 - Cyclone 3
 - O-15 generator, IBA, Belgium
 - MGC-20, positive ion
 - 40 μA , Efremov Institute, Russia
 - CC-18/9, negative ion
 - up to 100 μA , Efremov Institute, Russia



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Background – MGC-20







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Background – CC-18/9





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Background

– Specific Radioactivity, SA



$$SA = \frac{\text{Amount of radioactivity [Bq]}}{\text{Mass [mol]}} = \frac{A}{n}$$

■ Units: GBq/μmol
Ci/μmol

■ Mass = the total amount, including both the stable and the isotopically labelled portions

Nuclide	SA _{max} [Ci/μmol]
¹¹ C	9200
¹³ N	18800
¹⁵ O	92000
¹⁸ F	1700
³ H	0.029
¹⁴ C	0.000062
³² P	9.1

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Background

– Why high SA?



■ High SA [Bq/mol] = low mass

→ *Tracer principle*

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The Concept of a Radiotracer



Reindeer round-up and Marking, Kittilä, autumn 2003, Jouni Törmänen

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Background

– Why high SA?



■ High SA = low mass

→ *Tracer principle*

→ No over blocking due mass effect

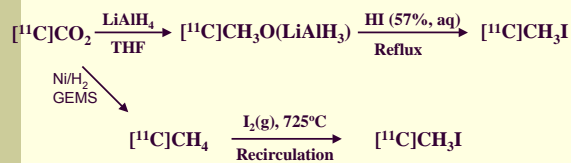
→ No pharmacological effects

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Background

– Labelled precursor production



- Classic method: $[^{11}\text{C}]\text{CO}_2$ / LiAlH_4 / THF / HI
 - Corrosive, highly flammable reagents
 - Sensitive to external CO_2 (air) → SA↓
- GEMS gas phase synthesis box
Larsen P, Ulin J, et al., *Appl Radiat Isot* **48**, 153-157, (1997)

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Aims



- Evaluate the new production method of $[^{11}\text{C}]\text{FLB 457}$ using
 - *In situ* produced $[^{11}\text{C}]\text{CH}_4$
 - Recirculating radical iodination to produce $[^{11}\text{C}]\text{CH}_3\text{I}$
 - Modified $[^{11}\text{C}]\text{CH}_4$ target*

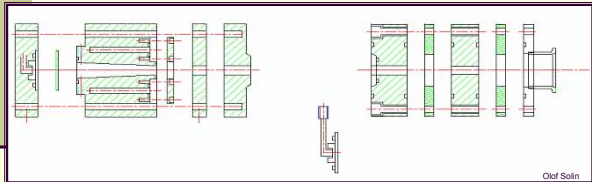
*) Björk H, Dahlström K, et al. Production of in-target ^{11}C on a specific activity optimized ^{11}C PET trace target, *10th Workshop on Targetry and Target Chemistry*, Madison (2004)

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Experimental – $[^{11}\text{C}]\text{CH}_4$ production target

$^{14}\text{N}(\text{p},\alpha)^{11}\text{C}$; N_2/H_2 ; 5-10% H_2

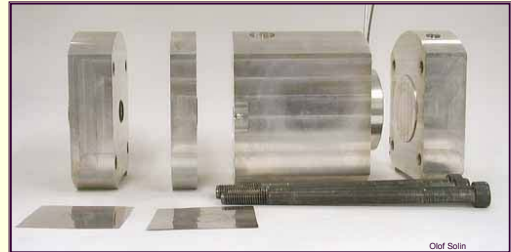


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Experimental – $[^{11}\text{C}]\text{CH}_4$ production target



Olof Solin

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Experimental – Reducing carbon sources

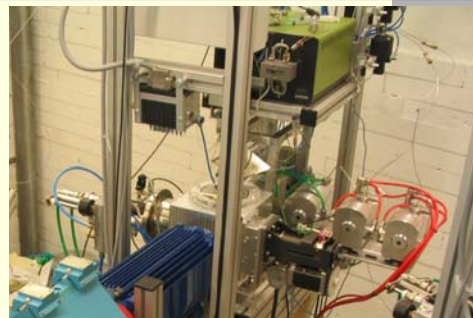


Olof Solin

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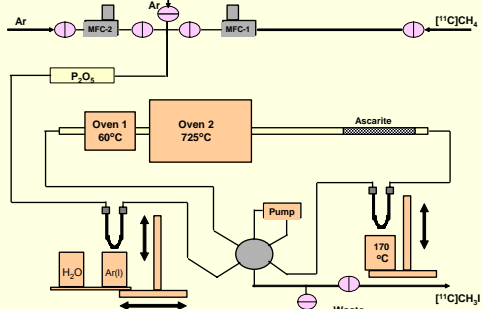
Experimental – Reducing carbon sources



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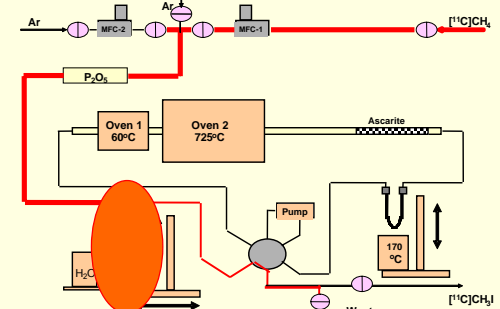
Experimental – $[^{11}\text{C}]\text{CH}_3\text{I}$ Production device



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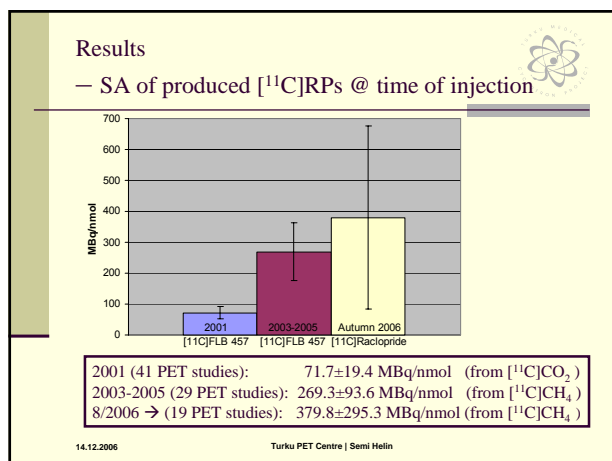
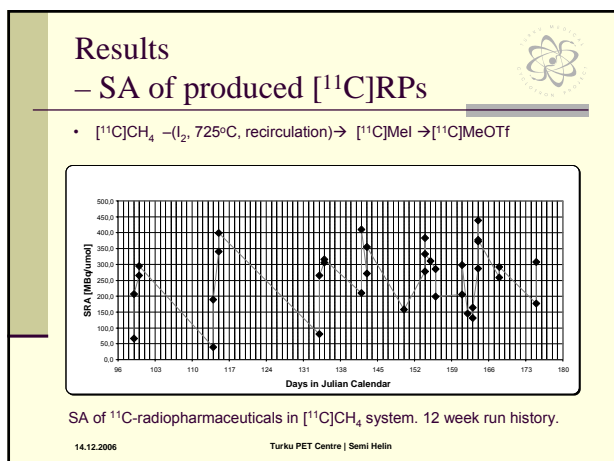
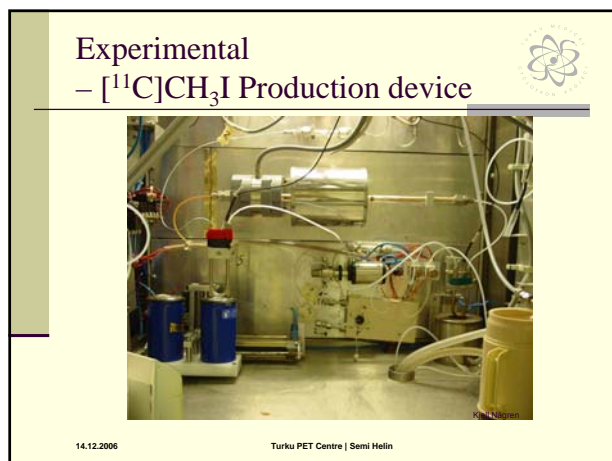
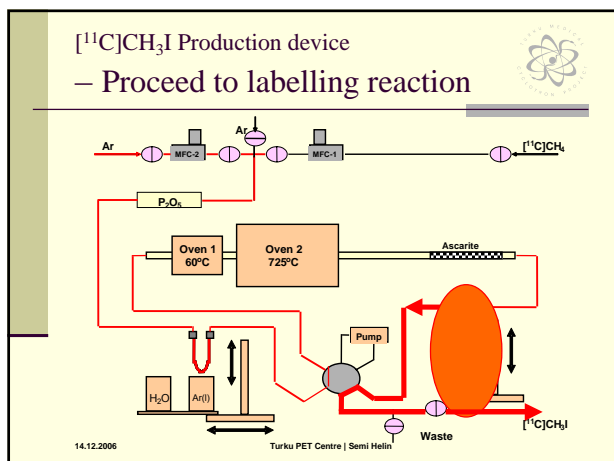
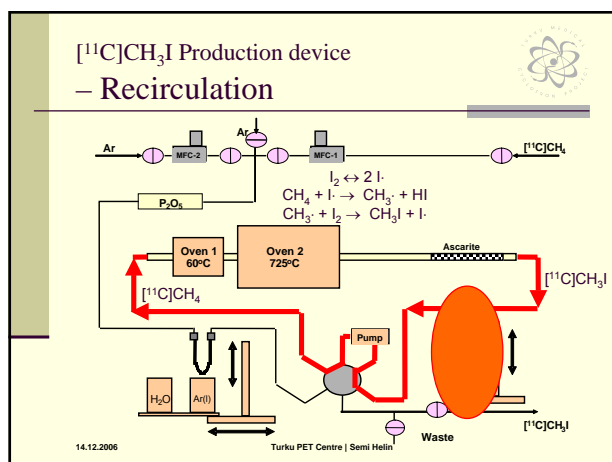
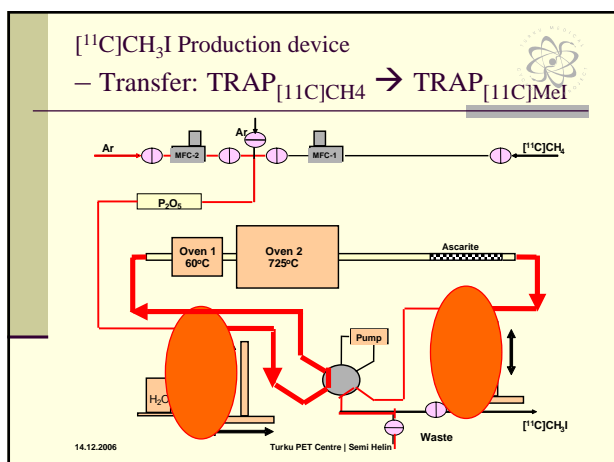
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$[^{11}\text{C}]\text{CH}_3\text{I}$ Production device – Trapping of $[^{11}\text{C}]\text{CH}_4$

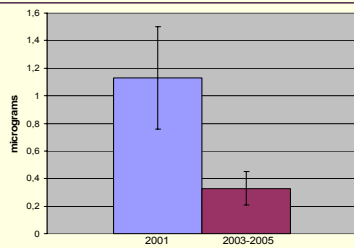


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Injected mass of [^{11}C]FLB 457 in human PET studies in Turku



2001 (41 PET studies): Injected $1.13 \pm 0.37 \mu\text{g}$ (from [^{11}C]CO₂)
 2003-2005 (29 PET studies): Injected $0.329 \pm 0.123 \mu\text{g}$ (from [^{11}C]CH₄)

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Summary & Conclusions



■ Turku, Stockholm and Japan

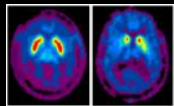
- specially designed targets
- *In situ* produced [^{11}C]methane
- re-circulating gas phase iodination

→ high specific radioactivity (400-4000 MBq/nmol) EOS
 (compare typical 40-400 MBq/nmol of [^{18}F]RCPs)

→ Mass 50-500 ng
 - studies with high-affinity ligands like [^{11}C]FLB 457

14.12.2006

Turku PET Centre | Semi Helin



Thank you



Recent applications of Helsinki's cyclotron

Stewart Makkonen-Craig

Laboratory of Radiochemistry, University of Helsinki

Cyclotron

The Laboratory of Radiochemistry, University of Helsinki, houses an IBA Cyclone 10/5 cyclotron. It accelerates protons to 10 MeV and deuterons to 5 MeV. Although designed primarily for the production of short-lived PET radionuclides, we use the cyclotron in a versatile way to meet the demands of our research groups, research collaborators and commercial partners. The cyclotron has also proved to be an excellent pedagogic tool when educating radiochemistry students on radionuclide production, radiation chemistry, radiation safety and accelerator principles.

Radionuclide production

The primary function of the cyclotron is production of PET radionuclide fluorine-18 for our radiopharmaceutical research team. They actively develop labelling methods of novel radiopharmaceuticals that target brain receptors expressed in neurodegenerative and psychiatric disorders. Fluorine-18 is also produced routinely in large quantities for the synthesis and distribution of [^{18}F]FDG by our commercial partner. Our external beamline permits implementation of solid and gas targetry, and we aim to exploit this capability by producing other PET radionuclides, e.g. copper-64 and carbon-11, in the near future.

Proton-induced nuclear reactions on uranium and transuranium targets have successfully yielded short-lived neptunium and plutonium nuclides that can act as geochemical and biological tracers. The experiments have generated new reaction cross-section data, and have been very popular for students learning about radionuclide production and actinide separation techniques.

Radiation chemistry

We have constructed a target system on the beamline for the irradiation of broad areas of polymer films. The novel objective is to manipulate solid-state polymers for the production of ion exchange and proton-conducting membranes, leading ultimately to affordable fuel cell membranes. Proton irradiation of polymer films produces rectilinear paths of radiolytic species. The radiolysis is then functionalised by sulfonation, yielding hydrophilic nanochannels that conduct ions. A spin-off from this research has been the development of polymer film dosimetry for lateral ion beam profiling and for demonstrating the Bragg curve to our students.

Name	Stewart Makkonen-Craig
Company / University	University of Helsinki
Web-page	www.mv.helsinki.fi/home/smakkone
Phone (direct line)	+358 9 191 50144
Fax	+358 9 191 50121
E-mail	stewart.makkonen-craig@helsinki.fi

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UNIVERSITY OF HELSINKI

Recent applications of Helsinki's cyclotron

Stewart Makkonen-Craig
YoungRad seminar
14.12.2006

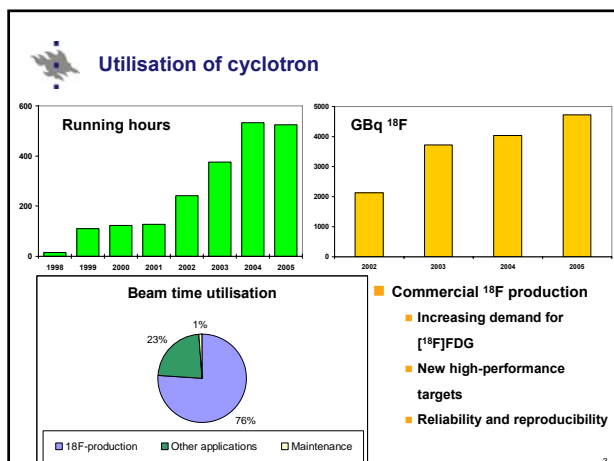
Laboratory of Radiochemistry, University of Helsinki

Recent applications of Helsinki's cyclotron

- Research**
 - Radionuclide production
 - Radiation chemistry
- Teaching**
 - All research projects
 - Unexpected technical failures in all major components
 - Student operation
- Commercial ^{18}F production**



IBA Cyclotron cyclotron 10 MeV p 5 MeV d




Transuranium tracer production

- $^{235,238}\text{Np}$ and $^{236,237}\text{Pu}$**
 - Geological and biological tracers
 - Not easily commercially available
- Production with < 10 MeV p**
 - Near Coulomb barrier
 - Direct or indirect
 - Quantify reaction cross-section at various p energies
- Practical course for undergraduates to post-docs**
 - Collaboration with Khlopin Radium Institute, St. Petersburg, Russia
 - Radionuclide production, ion exchange, α and γ spectrometries


Helsinki Molecular Imaging Center

radionuclide production




Cyclotron:
IBA cyclone 10/5
installed: 1998

chemical processing




F-18 modules:
Home made radiosynthesis modules

quality control



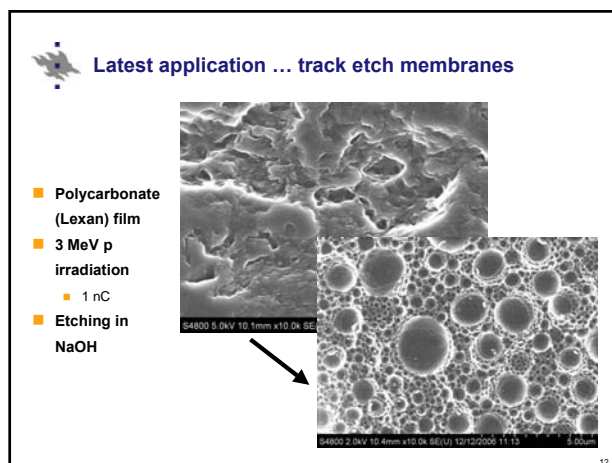
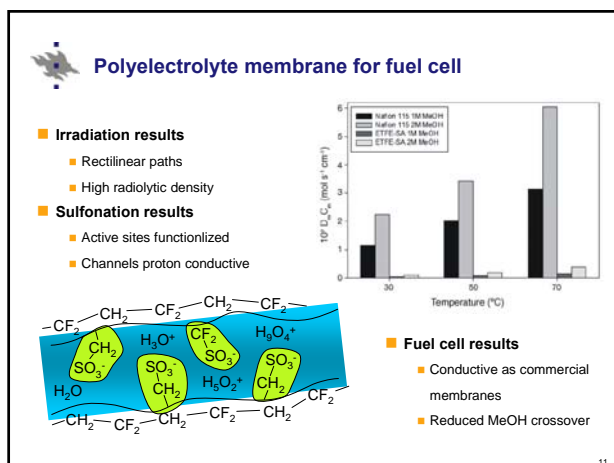
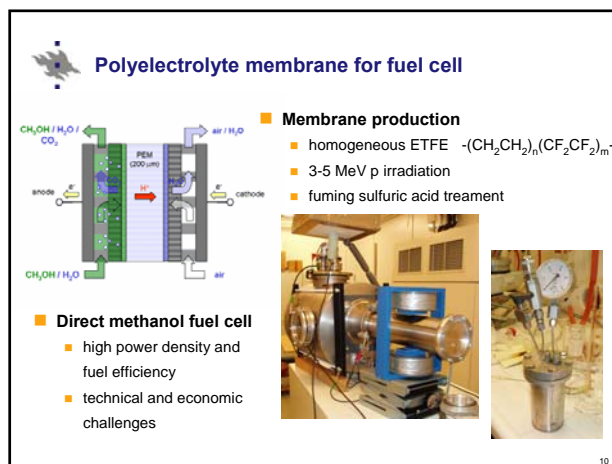
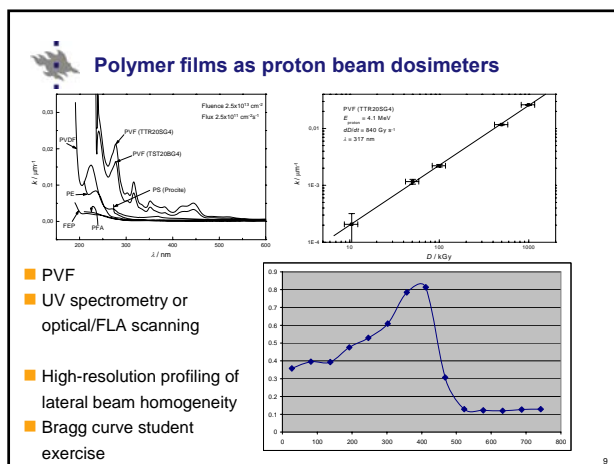
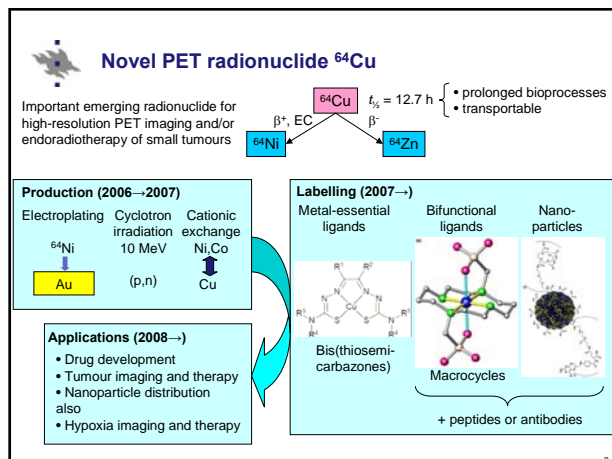
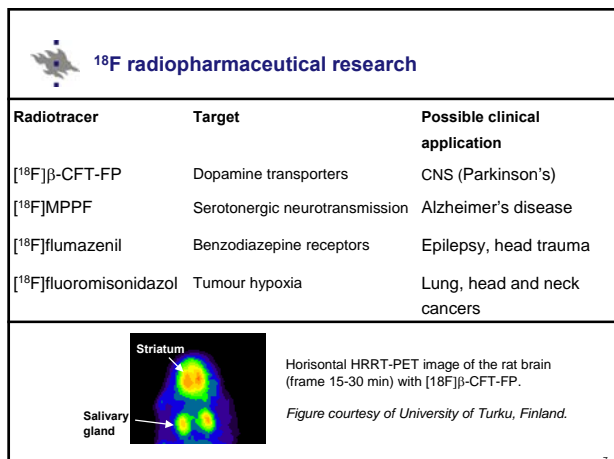
Methods:
TLC
HPLC
LC/MS
NMR

injection & scanning



Scanner (HUSLAB):
Philips Gemini PET/CT
Installed: 2006

Biomedical radionuclides with a 10/5 cyclotron





A case study of radiopharmaceutical production ($[^{18}\text{F}]\text{FDG}$) at the University of Helsinki.

Paintner Risto, Tuovinen Hanna, Lehto Jyri

MAP Medical Technologies Oy

This abstract describes the production of $[^{18}\text{F}]\text{FDG}$ at the Laboratory of Radiochemistry in collaboration with MAP Medical Technologies Oy, a private Finnish radiopharmaceutical company. All of the production steps are carried out routinely by chemistry students of the University of Helsinki.

The pharmaceutical end-product is used at several Scandinavian central hospitals as a marker in diagnostic PET-studies. $[^{18}\text{F}]\text{FDG}$ is a glucose derivative labelled with radionuclide ^{18}F . The glucose derivative is absorbed at metabolically active sites in the body, such as malignant tumours. ^{18}F decays by positron emission, which allows the PET camera to determine the exact location of these metabolically active sites in the body.

The manufacturing process starts with the production of the radioactive ^{18}F , which is produced by a cyclotron located at the University of Helsinki. After this, the active isotope is transferred to an automated synthesis module, where mannose-triflate is labelled by the active fluorine. Activities of a production batch can be as high as 120 GBq, so special attention in radiation protection is essential. After synthesis, the pharmaceutical product is processed in a clean-room facility and delivered to the hospitals by taxi or plane. The whole process, from start of synthesis till injection into the patient must be completed as quickly as possible due to the short, 110-minute half-life of ^{18}F .

Name	Risto Paintner
Company / University	MAP Medical Technologies Oy
Web-page	www.mapmedical.fi
Phone (direct line)	+358 9 191 50511
Fax	+358 9 191 50155
E-mail	risto.paintner@mapmedical.fi

A case study of radiopharmaceutical production ([¹⁸F]FDG) at the University of Helsinki



Hanna Tuovinen, Jyri Lehto, Risto Paintner
MAP Medical Technologies Oy

Introduction

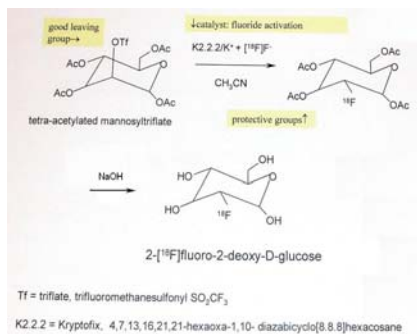
2-Deoxy-2-[¹⁸F]fluoro-D-glucose ([¹⁸F]FDG) is the most frequently used radiopharmaceutical for positron emission tomography (PET). The application of PET utilizing [¹⁸F]FDG in medical diagnosis has expanded dramatically over the last several years. It is estimated that there are now over 400 centers worldwide carrying out this diagnostic procedure.

The production of [¹⁸F]FDG at the Laboratory of Radiochemistry is carried out by MAP Medical Technologies Oy, a private Finnish radiopharmaceutical company. The production process is done in collaboration with The University of Helsinki. The Laboratory of radiochemistry provides the F-18 and MAP carries out the synthesis and pharmaceutical quality control.

Synthesis

The manufacturing process starts with the production of the radioactive ¹⁸F. It is produced by a cyclotron (IBA 10/5) situated in radiochemistry laboratory at the University of Helsinki. Activities of a production batch can be more than 100 GBq, so special attention in radiation protection is essential. The radioisotope is transferred from the target to an automated synthesis module, which is 15 meters away from the cyclotron. The transfer of fluorine through a teflon tube takes about 40-90 seconds.

We use the method of phase transfer catalysed nucleophilic substitution of 1,3,4,6-tetra-O-acetyl-2-O-trifluoromethanesulphonyl-β-D-mannopyranose with [¹⁸F]fluoride. [¹⁸F]fluoride is adsorbed on an anion-exchange resin and eluted with a solution of potassium carbonate which is then evaporated to dryness. Addition of phase transfer catalyst (kryptofix 2.2.2) in dry acetonitrile is used to enhance the nucleophilicity of the [¹⁸F]fluoride so that it reacts easily with the tetra-acetylated mannosyltriflate at elevated temperature. Hydrolysis under alkaline conditions yields 2-[¹⁸F]fluoro-2-deoxy-D-glucose. The final product is purified by serial chromatography.



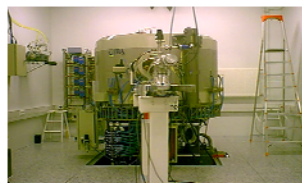
Distribution

After synthesis the final product is transferred to the clean room facility in a lead shield. The solution is divided into portions for the hospitals. The microbiological tests, the endotoxin test and a sample for the quality control are taken. After this the [¹⁸F]FDG in a multidose vial is packed appropriately and sent to the hospitals by taxi or aircraft.

Quality Control

To assure the quality and safety of [¹⁸F]FDG injection, quality checks must be performed for each batch of the product. Quality requirements are specified in the European Pharmacopoeia. The radiochemical purity, pH and appearance are determined. The final product is a clear, colourless or slightly yellow solution with pH ranging between 4.5-8.5. Radiochemical purity is tested with TLC. The radiochemical purity of [¹⁸F]FDG-solution should be over 95% and the Rf should be approximately 0.35-0.55. After approval of the product, the hospitals are given permission to administer the [¹⁸F]FDG to the patient.

Duration of irradiation
20-240 min



¹⁸F is produced by an IBA cyclotron. Heavy H₂¹⁸O water is bombarded with 10 MeV protons. ¹⁸O(p,n)¹⁸F

Duration of synthesis
25 min



Synthesis is carried out by an automated TRACERlab FX_{FDG} synthesiser.

Clean-room processing
25 min



After synthesis the product is processed in a clean-room facility

Packaging and labelling
15 min



The 15ml product vial is placed in a 22 kg lead shield for transportation.

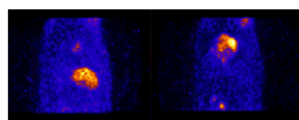
Quality Control
40 min



Delivery to the hospitals
20-180 min

Quality control is carried out while the product is transported to the hospital

PET-scan
25 min



FDG is used at several Scandinavian central hospitals as a marker in diagnostic PET-studies.

The whole process, from start of synthesis till injection into the patient must be completed as quickly as possible due to the short, 110 minute half-life of ¹⁸F.



¹⁸F-Radiochemistry in the University of Helsinki

Tiina Lipponen and Teija Koivula
Laboratory of Radiochemistry, University of Helsinki

Radiopharmaceutical chemistry is one of the main research and teaching areas in the Laboratory of Radiochemistry, University of Helsinki. This research field is largely based on our cyclotron, which is designed for the production of short-lived positron emitters, e.g. fluorine-18 and carbon-11. These radionuclides are used to label radiotracers for molecular imaging. The imaging method is called positron emission tomography (PET). At present we have focused on fluorine-18 chemistry. Our research concentrates mainly on developing ¹⁸F-labelled tracers in order to study the function of receptors in brain in neurodegenerative and psychiatric disorders.

We have developed a method for labelling a phenyl tropane analogue, N-(3-fluoropropyl)-2β-carbomethoxy-3β-(4-fluorophenyl)nortropane (β-CFT-FP) with fluorine-18. Radiolabelled cocaine analogues, like β-CFT and its derivatives, are used in the diagnosis of a variety of CNS (central nervous system) diseases such as Parkinson's disease. Three different labelling methods were tested and the approach using [¹⁸F]fluoropropyl tosylate as a labelling reagent was developed further [1]. [¹⁸F]β-CFT-FP was produced by this optimised method and the final product was used for preclinical studies in Turku PET Centre [2].

Synthesis of two other receptor ligands 4-[¹⁸F]fluoro-N-[2-[1-(2-methoxyphenyl)-1-piperazinyl]ethyl]-N-2-pyridinylbenzamide (p-[¹⁸F]MPPF) and ¹⁸F-labelled flumazenil has been studied. p-[¹⁸F]MPPF is a tracer for imaging serotonergic neurotransmission. Flumazenil is a ligand which binds to central benzodiazepine receptors. Changes in this receptor density have been demonstrated in epilepsy. Labelling methods for both tracers have been tested with respect to reaction parameters, such as stoichiometric conditions, reaction temperature and heating method, to improve the radiochemical yield of the final product. The synthesis procedures have been semi-automated.

We have also readiness for preparing following tracers, [¹⁸F]fluorothymidine ([¹⁸F]FLT) and [¹⁸F]fluoromisonidazole ([¹⁸F]FMISO). These tracers are used in cell proliferation studies in tumours: [¹⁸F]FLT, as a nucleoside analogue, for the synthesis of nucleic acids and [¹⁸F]FMISO for hypoxia studies. The synthesis of [¹⁸F]FMISO is adapted to an automated module [3].

In developing synthesis procedures we have used several qualitative and quantitative analytical methods to determine the purity of the final product and to identify side-products. Radiolabelling yields were measured by TLC (thin layer chromatography) and results were verified by HPLC (high pressure liquid chromatography). Products and impurities were identified by LC-MS (liquid chromatography-mass spectrometry) when needed.

References

- 1) Koivula T. et al. J Label Compd Radiopharm 2005; 48: 463-471
- 2) Koivula T. et al. submitted to Nucl Med Biol
- 3) Kämäräinen EL. et al. J Label Compd Radiopharm 2004; 47: 37-45

Name	Tiina Lipponen
Company / University	University of Helsinki
Web-page	www.helsinki.fi/kemia/radiokemia
Phone (direct line)	+358 9 191 50134
Fax	+358 9 191 50121
E-mail	tiina.lipponen@helsinki.fi

¹⁸F-RADIOCHEMISTRY IN THE UNIVERSITY OF HELSINKI

[¹⁸F]β-CFT-FP We have developed a method for labelling a phenyl tropane analogue, *N*-(3-fluoropropyl)-2β-carbomethoxy-3β-(4-fluorophenyl)nortropane (β-CFT-FP) with fluorine-18. Radiolabelled cocaine analogues, like β-CFT and its derivatives, are used in the diagnosis of a variety of CNS (central nervous system) diseases such as Parkinson's disease. Three different labelling methods were tested and the approach using [¹⁸F]fluoropropyl tosylate as a labelling reagent was developed further¹. [¹⁸F]β-CFT-FP was produced by this optimised method and the final product was used for preclinical studies in Turku PET Centre².

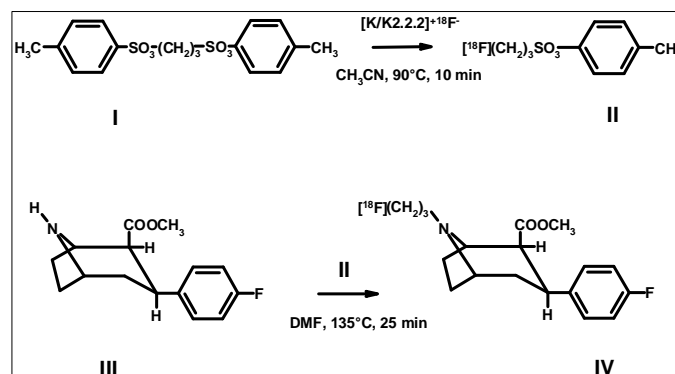


Figure 1. Synthesis of [¹⁸F]fluoropropyl tosylate (II) and radiolabelling of [¹⁸F] β-CFT-FP (IV) starting from nor-β-CFT (III).

***p*-[¹⁸F]MPPF** Radiolabelling of 4-[¹⁸F]fluoro-*N*-[2-[1-(2-methoxyphenyl)-1-piperazinyl]ethyl]-*N*-2-pyridinyl-benzamide (*p*-[¹⁸F]MPPF), a ligand for imaging of serotonergic 5-HT_{1A} neurotransmission with positron emission tomography (PET), has been studied. The aim of our study has been to improve the radiolabelling yield of *p*-[¹⁸F]MPPF and especially, to study the reaction mechanism and identify the radiolabelled side products in the synthesis.

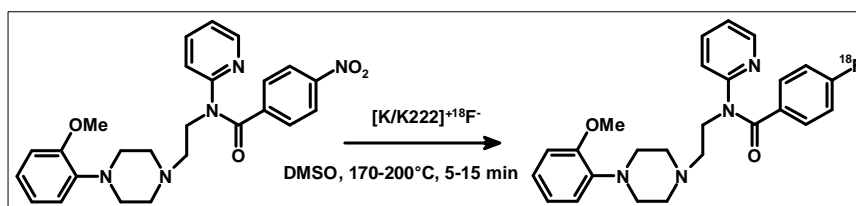


Figure 2. Synthesis of *p*-[¹⁸F]MPPF.

[¹⁸F]FMZ Flumazenil is a ligand which binds to central benzodiazepine receptors. Changes in this receptor density have been demonstrated in epilepsy. The synthesis method has been tested with respect to reaction parameters, such as stoichiometric conditions, reaction temperature and heating method.

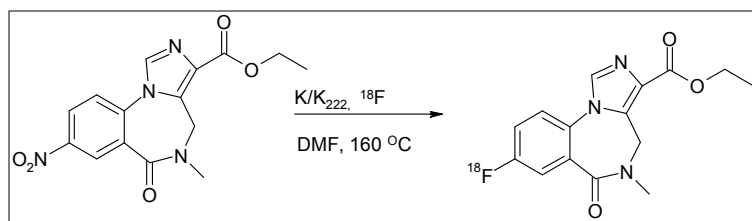


Figure 3. Synthesis of [¹⁸F]FMZ.

We have also readiness for preparing [¹⁸F]fluorothymidine ([¹⁸F]FLT) and [¹⁸F]fluoromisonidazole ([¹⁸F]FMISO)³. These tracers are used in cell proliferation studies in tumours: [¹⁸F]FLT, as a nucleoside analogue, for the synthesis of nucleic acids and [¹⁸F]FMISO for hypoxia studies. All synthesis procedures have been semi- or fully-automated. In developing labelling procedures we have used TLC (thin layer chromatography) and HPLC (high pressure liquid chromatography) as analytical methods. In some cases also LC-MS (liquid chromatography-mass spectrometry) has been used for identifying final product and possible labelled impurities.

References

- 1) Koivula T. *et al. J Label Compd Radiopharm* 2005; 48: 463-471
- 2) Koivula T. *et al. submitted to Nucl Med Biol*
- 3) Kämäräinen EL. *et al. J Label Compd Radiopharm* 2004; 47: 37-45

SESSION III

Environmental Radioactivity and Applications

Oral presentations

Elisabeth Strålberg

Activities at the Environmental Monitoring Section at Institute for Energy Technology (IFE), Norway

Mohamad Zakaria

“Atoms for peace”? Nuclear Energy and Peace

Ole-Christian Lind, B. Salbu, L. K. Klausen, K. Janssens, K. Proost, B. Vekemans

Radioactive Particles Originating from Events Involving Nuclear Weapons

Sven K. Hartvig, T. Bjørnstad

Radioactive Tracers for Oil Reservoirs - Concept, Tracers and Analysis

Roongrat Petersen

Chemical Fractionation of Pu and Am in Soils and Sediments: Readsorption Study

Poster presentations

Jarkko Ylipieti, D. Solatie

Trends and Correlations in ^{137}Cs Concentrations in the Fish Fauna of the Lake Apukkajärvi in Finnish Lapland

Kaisa Vaaramaa, J. Lehto

Soluble and Particle-bound ^{238}U -series Radionuclides in Ground Waters

Miia H. Palosaari

Detection of Irradiated Foods by the Thermoluminescence of Mineral Contamination

Mervi Söderlund, Lalli Jokelainen and Kerttuli Helariutta¹

Practical course on radionuclide production

¹ The presentation was registered after the official deadline and was therefore not included in the agenda for the seminar.



Activities at the Environmental monitoring Section at Institute for Energy Technology (IFE), Norway

Elisabeth Strålberg

Institute for Energy Technology (IFE), P.O.BOX 40, NO-2027 Kjeller, Norway

The Health and Safety Department at IFE is responsible – at the Kjeller site – for IFE's institute level activities in the fields of health-safety-environment (HSE), radiation protection and environmental monitoring. IFE's health and safety personnel have a professionally free and independent position in all matters of health, safety and working environment. They assist the management as well as the employees, the site Safety Officers, the Safety Committee, and the Working Environment Committee in such matters.

The Environmental Monitoring Section at the Health and Safety Department is responsible for

- monitoring of discharges of radioactivity to air and water from IFE's nuclear activities at Kjeller so that these do not exceed the limits given by the Norwegian Radiation Protection Authority (NRPA)
- monitoring the levels of radioactivity in the local environment around IFE
- performing urine analyses of personnel in co-operation with the Radiation Protection Section at the Department.

In addition the Section participates in relevant national and international research projects and provides analytical and other services for authorities, industry and others within its fields of competence.

The Environmental Monitoring Section operates one of the largest laboratories in Norway for radiochemical analyses and measurement of radioactivity in all kinds of materials.

This presentation will give an overview of the main ongoing activities at the Section.

Name	Elisabeth Strålberg
Company / University	Institute for Energy Technology
Web-page	www.ife.no
Phone (direct line)	+47 63 80 60 95
Fax	+47 63 81 25 61
E-mail	elisas@ife.no

Activities at the Environmental Monitoring Section at Institute for Energy Technology (IFE), Norway

Elisabeth Strålberg

Institute for Energy Technology
P.O.Box 40, 2027 Kjeller, Norway

YoungRad seminar, Helsinki, 14-15 December 2006

15.01.2007



Institute for Energy Technology

- Independent foundation, established in 1948
- 550 employees (Kjeller and Halden)
- Main activity areas
 - Nuclear Technology (Kjeller)
 - Petroleum Technology (Kjeller)
 - Energy, Environmental Technology and Physics (Kjeller)
 - Safety – MTO (Man-Technology-Organisation) (Halden)
 - Nuclear Safety and Reliability (Halden)

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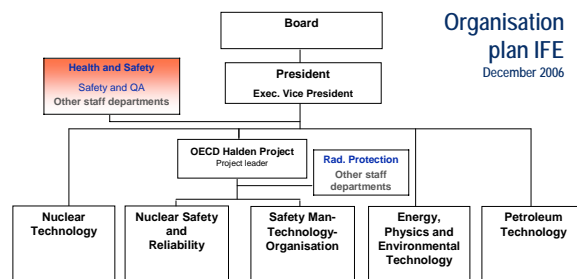
Health and Safety Department

- Responsible – at the Kjeller site – for IFE's institute level activities in the fields of health-safety-environment (HSE), radiation protection and environmental monitoring
 - IFE's health and safety personnel have a professionally free and independent position in all matters of health, safety and working environment. They assist the management as well as the employees, the site Safety Officers, the Safety Committee, and the Working Environment Committee in such matters.
- Research and assessment activities in its fields of competence, which also includes radioactive waste management

15.01.2007



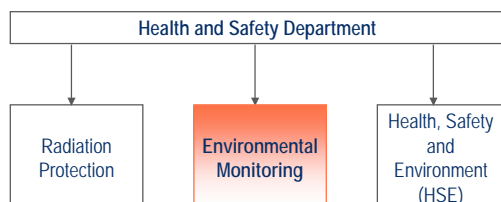
Organisation plan IFE December 2006



15.01.2007



Environmental Monitoring Section



15.01.2007



Environmental Monitoring

- Monitoring of discharges of radioactivity to air and water from IFE's nuclear activities at Kjeller so that these do not exceed the limits given by the Norwegian Radiation Protection Authority (NRPA)
 - Discharge limit to air: 100 μ Sv per year (not more than 10 μ Sv per year for isotopes of iodine)
 - Discharge limit to water: 1 μ Sv per year
- Monitoring the levels of radioactivity in the local environment around IFE
- Performing urine analyses of personnel in co-operation with the Radiation Protection Section
- Relevant radionuclides: ^3H , gamma emitters, ^{90}Sr , ^{238}Sr , ^{239}Pu , ^{240}Pu , ^{241}Am , uranium

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Discharges to air

- Air filters at discharge points
 - weekly
- Air filters monitoring outside air
 - weekly, 2 locations at IFE
- Rain water
 - quarterly, 5 locations at IFE
- Grass
 - 4 times a year (summer), 11 locations at and close to IFE
- Milk
 - Weekly, 2 locations (local farms)
- Agricultural products
 - once a year, 2 locations (local farms)



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Control of the NALFA pipeline

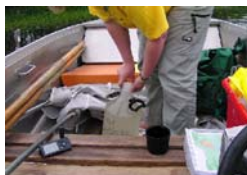
- All waste water is discharged through the NALFA (Ny Avfallsledning for Lavaktivt Flytende Avfall) pipeline to the local river Nitelva
- Control of leakage from the NALFA pipeline is performed once a year
 - Samples of water and sediment/sand collected from all manholes along the pipeline

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Discharges to water

- All waste water is transferred to large tanks (appr. 30 m³) and a sample is collected and analysed before discharge permit is given
 - appr. 5 times a year
- Water samples from the river Nitelva
 - 3 times a year (summer), 6 locations
- Sediment samples from the river Nitelva
 - Yearly (during summer), 6 locations
- Fish
 - Twice a year (summer), 1 location
- Aquatic plants
 - Twice a year (summer), 1 location



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Himdalen

- IFE operates the national, combined storage/disposal facility for radioactive waste in Himdalen
- Yearly control of
 - Drainage water
 - Surface water (two small lakes close to the facility)
- Extended control every five years
 - Surface water, ground water
 - Sediment, bog
 - Biota (pine, birch, blueberries, lichen...)
 - Elk

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Urine analyses

- Monitoring of personnel is performed by the Radiation Protection Section
- Urine samples from relevant personnel collected 4 times a year
 - Analysed mainly for ³H,
 - ...but also ⁹⁰Sr, Pu, Am and U



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EU projects

- Now: positioning for EU's FP 7
- No participation in EU's FP 6
- Participation in EU's FP 4 and 5
 - **REMOTRANS** - Processes Regulating Remobilisation, Bioavailability and Translocation of Radionuclides in Marine Sediments
 - **ECOPRAQ** - Modelling Fluxes and Bioavailability of Radiocaesium and Radiostrontium in Freshwaters
 - **ARMARA** - Radioecological assessment of the consequences of contamination of Arctic waters: modelling the key processes controlling radionuclide behaviour under extreme condition
 - **SUCON** - Radiological assessment of past, present and potential sources to environmental contamination in the Southern Urals and strategies for remedial measures

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NFR projects

(NFR – Norwegian Research Council)

- **RAIV** - Radioactivity in Produced Water from Norwegian Oil and Gas Installations – Concentrations, Bioavailability and Doses to Human and Marine Biota
 - Main objective:
 - Establish radiological safe discharge limits for radium, lead and polonium associated with other components in produced water from oil and gas installations on the Norwegian continental shelf
 - Some sub-objectives:
 - Establishing natural background levels of the relevant radionuclides
 - Assessing leakage from sediment as a source of radium
 - Study mobility, sedimentation mechanisms, bioavailability and bioaccumulation of the radionuclides given different discharge scenarios

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NKS projects

- Ongoing:
 - **FOREST** - Guidance for Sampling in Forests for Radionuclide Analysis and Update of the Nordic Radioecology Network
 - Prepare a sampling guide for radionuclide analysis of northern forests to improve accuracy, reliability and comparability of data. Thereby the reliability of model parameters derived from the data, and assessment of radiation doses after radiological accidents will also be improved.
 - To form a network for Nordic forest radioecologists
 - **HOT** - Radioactive Particles in a Nordic Context
 - Increasing the awareness of problems and possibilities associated with radioactive particle contamination
 - Publish a review report and a database on sources and characteristics of radioactive particles
- Completed:
 - **INDOFERN** - New Indicator Organisms for Environmental Radioactivity
 - **RADCHEM** - Radiochemical Analysis in Emergency and Routine Situations
 - +++

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Other projects

- Radioactivity in seaweed
 - Study of radioactivity along the Norwegian coast (time series since 1980 of brown algae samples)
- AMEC
 - Cooperation between USA, Russia, Norway and UK
 - The purpose of the programme has been to assist Russia with technological solutions for solving defense-related environmental problems in the Arctic areas
 - Norway and USA pulled out of the cooperation in 2006

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NORM related services

- Produced water
 - Goal set by the OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic:
 - Concentrations in the environment near background values for naturally occurring radioactive substances and close to zero for artificial radioactive substances
 - NRPA has instructed the Norwegian oil and gas industry to collect samples of produced water at the point of discharge four times a year
 - The samples are to be analysed for ^{226}Ra , ^{228}Ra and ^{210}Pb
 - Most companies (if not all?) on the Norwegian continental shelf send samples to IFE

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NORM related services

- LSA Scale
 - Classification limits set by the NRPA: 10 Bq/g for each of the three radionuclides ^{226}Ra , ^{228}Ra and ^{210}Pb
 - Oil and gas companies send samples to IFE for classification
- Radon in building sites
 - Field measurements
 - Sampling and analyses of radon in soil air
 - HPGe analyses of natural radioactivity in rock

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NORM related services

- Assessments and classification of waste from different industrial processes
 - Uranium in cathode sludge from Magnesium production
 - Radium in LSA scale and sludge from oil and gas production (decommissioning of platforms, tanks etc..)
 - Uranium and thorium in waste from Niobium production
- Pre-concentration of radium from LSA scale and sludge
- Several reports on radioactivity in produced water, on request from authorities and industry
- Analytical services in connection to the coming repository for LSA scale waste

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Other analytical services

- Foodstuff and feeding stuff
 - Mainly gamma emitters and ^{90}Sr
- Seawater
 - Mainly ^{90}Sr , but also natural radioactivity
- Other environmental samples
 - Most radionuclides and activity levels
 - On request from both authorities and industry

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Quality assurance

- Quality assurance manual
- Regular participation in intercomparison exercises
 - IAEA, NIST, NPL, NKS...
- Qualified member of the IAEA ALMERA network
 - ALMERA = Analytical Laboratories for the Measurement of Environmental Radioactivity
 - Established by the IAEA in 1995
 - Purpose: to make available to all Member States a world-wide network of analytical laboratories capable of providing reliable and timely analysis of environmental samples in the event of an accidental or intentional release of radioactivity
 - Regular proficiency test for all qualified laboratories
- Internal revisions
- External revisions

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Thank you for your attention!



15.01.2007





Title: “Atoms for Peace”? Nuclear Energy and Peace

Authors: Mohamad Zakaria

Malmö Högskola; Lund University Centre for Sustainability Studies (LUCSUS), Lund University, Sweden.

Nuclear power plants and their role in sustaining peace or threatening it will be analysed. Nuclear energy contributes to the economic development of the country it is built in by providing electricity with cheaper prices than that of other kinds of energy. However, the construction costs of nuclear power plants are very expensive and it is a potential threat for human health and the environment. Different arguments on how nuclear power plants might contribute to peace or threaten it are analysed. The analysis is done mainly through Johan Galtung’s “Violence, Peace, and Peace Research” and “Cultural Violence” peace theories, as well as by recalling the different known nuclear accidents and mainly the one in the Chernobyl nuclear power plant. Cooperation of different stakeholders at national, regional, and international level is among the important tools to minimise the possibility of nuclear threat to peace. Nuclear waste and the uncertainties in best practices for the safe management is most probably the most severe problem that future generations will have to face.

Key words: peace; threat; cooperation; energy; risk; nuclear waste;sustainability.

Name	Mohamad Zakaria
Company / University	Malmö University
Web-page	www.mah.se
Phone (direct line)	+46 730295250
E-mail	mohamad.zakaria.868@student.lu.se

Nuclear Energy and Peace

By: Mohamad Zakaria

Peace and Conflict Studies Programme
PACS, International Migration and Ethnic Relations Division (IMER),
Malmö Högskola
&
Lund University Centre for Sustainability Studies (LUCSUS), Lund University,
Sweden

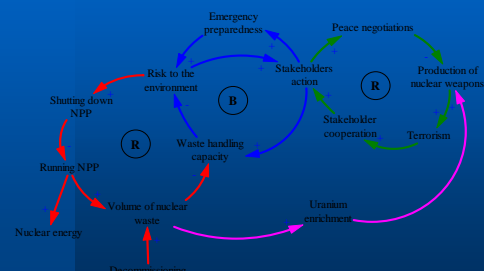
Some Facts regarding NP's

- Nuclear energy generates of about 15% of world's electricity
- Over 75% of nuclear reactors are found in the OECD countries
- Nuclear energy is characterised by very high initial costs but low running cost
- Economic useful life of reactors is about 25 years

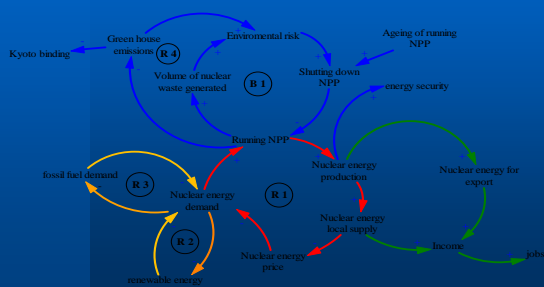
Objectives

- To show the negative impacts of nuclear energy on sustainability and peace
- To stress that there are some positive aspects of nuclear energy
- Highlight the problem of nuclear waste management

CLD for impact of nuclear energy on peace and the enviroment



CLD assessing socio-economic impacts of nuclear energy



Negative aspects of NPP

- Proliferation
- Pollution
- Nukes and terrorism
- Civil liberties
- Health risks
- Radioactive waste and decommissioning
- Nuclear accidents

Positive aspects of nuclear energy

- Promotes economic stability and energy security
- It significantly contributes to lowering CO₂ emission from energy sectors

How to reduce the impacts of NPP?

- Improve safety measures inside the NPP's to avoid nuclear accidents
- Cooperation of different stakeholders
- Implementation of sound national and international nuclear waste management policies

Some policy thoughts

- Not to shut down NPPs simultaneously, but gradually
- Find alternative technology for energy production
- Improve the role of International Atomic Energy Agency in supervising NPP's

Thank You!

Radioactive particles originating from events involving nuclear weapons



Ole-Christian Lind, Brit Salbu, Lotte Kjerre Klausen

Norwegian University of Life Sciences (UMB), Dep. of Plant- and Environmental Sciences, P.O.Box 5003, N-1432 Å, Norway

Koen Janssens, Kristof Proost, Bar Vekemans

University of Antwerpen, Dep. of Chemistry, Universiteitsplein 1, B-2610 Antwerp, Belgium

Since the beginning of the nuclear age the environment has been contaminated by radionuclides from more than 2300 atmospheric, surface, underground and underwater nuclear weapon tests and sub-critical safety trials (UNSCEAR, 1993). In addition, it is believed that at least 230 accidents have occurred involving the nuclear weapons of the US, the Former Soviet Union (FSU) and the UK between 1950 and 1980 (Gregory and Edwards, 1989). A significant fraction of refractory radionuclides released by nuclear events including nuclear weapons tests and nuclear weapon accidents have been shown to be associated with particles (Lind, 2006). To assess short- and long-term consequences of radionuclides released to the environment, information on the distribution of radionuclide species influencing mobility and biological uptake is essential. Particularly, impact assessment of particle contaminated ecosystems requires information on particle characteristics such as size, structure and oxidation state influencing weathering and mobilisation of matrix and/or associated radionuclides.

Previous studies of radioactive particles released from different nuclear sources and under different release conditions such as reactor accidents involving explosions or fires demonstrate that the particle characteristics are source and release scenario dependent. In the present work, radioactive particles collected from Semipalatinsk (FSU nuclear weapons test site), Palomares and Thule (accidents involving US nuclear weapons) have been characterised. Particles were isolated from soil and sediment samples using digital phosphor imaging or by gamma spectrometry and sample splitting. The isolated samples were further subjected to SEM and XRMA analysis for characterisation of structure and elemental composition and distribution. The next step was to analyse individual particles by means of synchrotron radiation based μ -X-ray fluorescence (μ -SRXRF), which is complementary to EM-techniques and is advantageous because of the sensitivity, low energy deposition, relatively large sampling depth and multi-elemental aspect. Micro-tomography were utilised to obtain info on porosity whereas micro-XRD shed light on crystallographic microstructures and micro-XANES reveal the oxidation state distributions. Following solid state characterisation selected single particles were sacrificed for radiochemical separations and mass spectrometry to provide isotope ratio information on the composition of the fissile material.

As observed for radioactive particles originating from various other sources released by different scenarios, radioactive particles originating from events involving nuclear devices at Semipalatinsk, Palomares and Thule are also source-related and release dependent.

References

Gregory, S. and Edwards, A., 1989. The Hidden Cost of Deterrence - Nuclear-Weapons Accidents 1950-88. Bulletin of Peace Proposals 20, 3-26.

Lind, O.C., 2006. Characterisation of radioactive particles in the environment using advanced techniques, PhD thesis, Norwegian University of Life Sciences, 1-191.

UNSCEAR, 1993. Sources and effects of ionizing radiation, United Nations, 1-922.

Name	Ole-Chritian Lind
Company / University	Norwegian University of Life Sciences (UMB)
Web-page	http://www.umb.no/ipm
Phone (direct line)	+47 64 96 55 45
Fax	+47 64 94 83 59
E-mail	ole-christian.lind@umb.no

RADIOACTIVE PARTICLES ORIGINATING FROM EVENTS INVOLVING NUCLEAR WEAPONS

Ole Christian Lind, Brit Salbu, Lotte Kjerre Klausen, Koen Janssens, Kristof Proost, Bart Vekemans



RADIOACTIVE PARTICLES – DEFINITIONS

Releases of anthropogenic radionuclides in various forms commenced with the nuclear era
One important form is so called radioactive particles

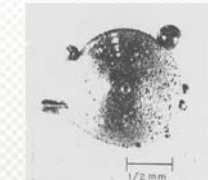
"Radioactive particles are defined as localised aggregates of radioactive atoms that give rise to an inhomogeneous distribution of radionuclides significantly different from that of the matrix background" (International Atomic Energy Agency (IAEA) CRP, 2001)

- Aquatic environment: $>0.45 \mu\text{m}$ (IAEA CRP, 2001)
- Aerosol particles in air: $1 \text{ nm} - 100 \mu\text{m}$ (Manahan, 1994)

SOURCES OF RADIOACTIVE PARTICLES NUCLEAR EXPLOSIONS AND SAFETY TESTS



Main source: 543 atmospheric nuclear weapon test sites (AMAP, 1998)

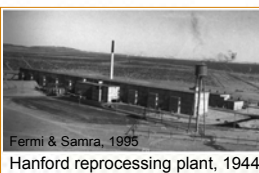


Particle from Nevada test site (Crocker et al., 1966)



Peaceful underground nuclear explosions (PUNE) in Russia (AMAP, 1998)

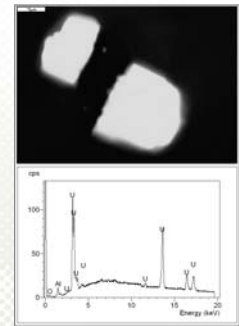
SOURCES OF RADIOACTIVE PARTICLES RELEASES FROM REPROCESSING PLANTS AND PRODUCTION SITES FOR WEAPON GRADE PU



Fermi & Samra, 1995

Hanford reprocessing plant, 1944

- Particles observed at several sites, for example:
 - Hanford and Rocky Flats, USA
 - Mayak PA, Tomsk and Krasnoyarsk, RUSSIA
 - Dounreay and Sellafield, UK



U fuel particle, Ravensglass, Irish Sea

SOURCES OF RADIOACTIVE PARTICLES NUCLEAR ACCIDENTS



Reactor accidents:
Windscale, Chernobyl (up to 10^5 particles/ m^2)



Nuclear weapon accidents: McGuire air force base, Johnston At., Palomares, Thule



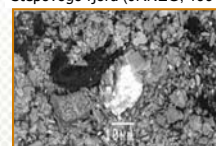
Satellite accidents

- Re-entry to earth's atmosphere of satellites with radioisotope thermoelectric generator (RTG)
 - SNAP 9A US satellite (1964)
- or nuclear reactors
 - Cosmos 954 Soviet satellite (1978)
 - Cosmos 1402 Soviet satellite (1983)

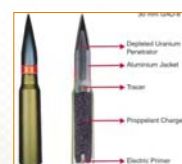
SOURCES OF RADIOACTIVE PARTICLES DUMPING OF NUCLEAR WASTE AND USE OF DU AMMUNITIONS



Dumped containers located in the inner parts of the Stepovogo fjord (JRNEG, 1994)



Radioactive particle in Stepovogo Fjord sediments, Novaya Zemlya (JRNEG, 1994)



IAEA, 2003

Use of DU ammunitions in testing ranges and conflicts: Gulf war, Balkan conflict, Iraq war

Characterisation of radioactive particles in the environment using advanced techniques
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IMPACT OF RADIOACTIVE PARTICLES SHORT TERM

- Radioactive particles can be subject to atmospheric transport
- Problems within micro-dosimetry
 - Skin dose
 - Inhalation- transmembrane uptake
 - Ingestion via food – retention times in the gastrointestinal tract
- Underestimated total inventory of radioactive contamination:
 - Inhomogeneous distributions– problems with representative sampling
 - Incomplete dissolution – measuring too low concentrations
- Problems with effective countermeasures
 - Often designed for ionic species

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IMPACT OF RADIOACTIVE PARTICLES LONG TERM

- Uncertainties in dose-estimates
- Problems within micro-dosimetry associated with resuspension: inhalation - ingestion
- Transformation processes $f(t)$
 - Weathering rates and remobilisation
 - Underestimation of transfer factors for ecosystems and environmental effects in particle contaminated areas (change in speciation, K_d and CF)

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ENVIRONMENTAL IMPACT ASSESSMENT MODELS – INFO NEEDED

Information on Becquerels is not enough!

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METHODS

- Sample preparation include digital autoradiography (identification of heterogeneities) and sample splitting/gamma measurements
- Scanning Electron Microscopy (SEM) and Environmental SEM (ESEM) with x-ray microanalysis (XRMA)
 - Identification, surface structure and elemental composition
- Synchrotron radiation (SR) based x-ray micro techniques
 - SR-based μ -XRF (micro X-ray fluorescence)
 - Subsurface elemental composition and distribution
 - SR-based μ -XANES (micro X-ray absorption near edge structure spectrometry)
 - Oxidation state determination
 - SR-based μ -XRD (micro X-ray diffraction)
 - Crystallographic forms
 - μ -tomography
 - Spatial distribution of structure and oxidation states
- Dissolution, radiochemical separations, mass spectrometry

Characterisation of radioactive particles in the environment using advanced techniques
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SCREENING FOR HETEROGENEITIES DIGITAL AUTORADIOGRAPHY

- Drying at room temperature to avoid altering the speciation

- Reusable image sensor (Imaging Plate, Molecular Dynamics)
- 10-100 times higher sensitivity than conventional X-ray or alpha radiation sensitive film
- 50-200 μ m resolution

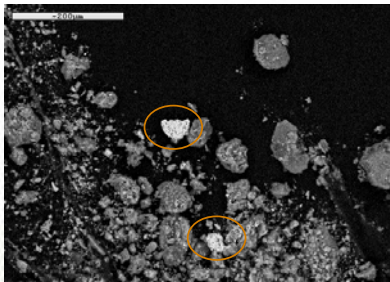
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ISOLATION OF RADIOACTIVE PARTICLES SAMPLE SPLITTING COMBINED WITH γ -SPECTROMETRY

Isolation of U/Pu particles from Palomares soils (García-Tenorio et al., EU ADVANCE, 2003)

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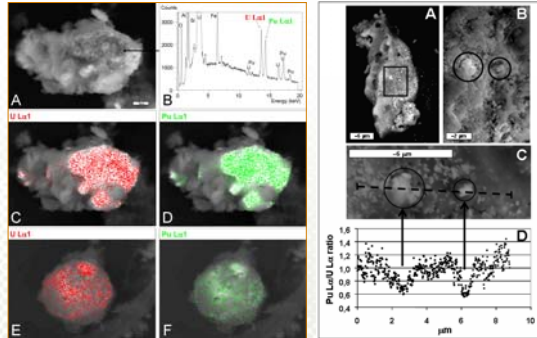
IDENTIFICATION IN SEM/ESEM (BEI)



- Backscattered Electron Imaging (BEI) mode
 - Bright areas reflect high average atomic number elements

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PARTICLE CHARACTERISATION: ELECTRON MICROSCOPY



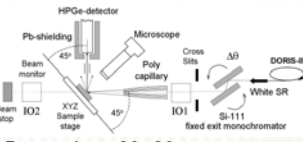
SEM x-ray mapping indicating homogeneously mixed U and Pu

ESEM x-ray line scan analysis reveal inhomogeneities in Palomares Pu/U particle

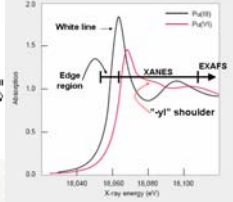
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SYNCHROTRON EXPERIMENTS BL, HASYLAB

XRF and XANES



Beam size ~20×20 μm



XANES

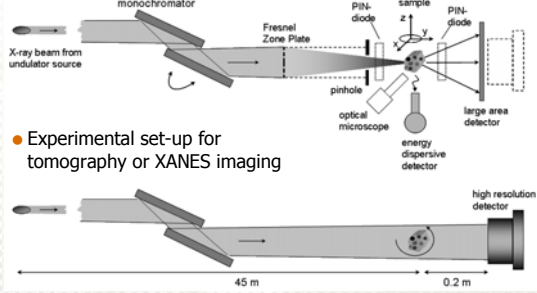
- Measure changes in the absorption coefficient $\mu(E)$ as a function of the incident radiation x-ray energy: $\log(I_0/I_t) = \mu \times d$
- Tuning the X-ray energy over the absorption edge (U L_{III}/Pu L_{III})
- Charge on the actinide atom influence edge position
 - Increased ox. state → increased absorption edge energy
- Information on the oxidation state of the matrix (U and Pu)
 - Based on white line/edge position and spectrum shape

Characterisation of radioactive particles in the environment using advanced techniques
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SYNCHROTRON EXPERIMENTS ID22, ESRF

RESOLUTION: 1 μm SCALE


- Experimental set-up for absorption (or fluorescence), XANES, diffraction (similar set-up at ID18)
- Experimental set-up for tomography or XANES imaging



Characterisation of radioactive particles in the environment using advanced techniques
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SEMIPALATINSK

NUCLEAR DEVICE TESTS (456 during 1949-1989)



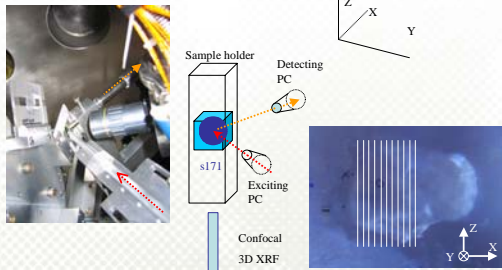
TEL'KEM CRATER LAKE

- Tel'kem I and II: U, Pu and ²⁴¹Am incorporated in large grains of soil (not vitrified)
- Ground zero and Balapan: Vitrified particles from high temperature scenarios
- Tel'kem (underground nuclear tests):
 - SEM-XRMA: No U, Pu signals on the surface
 - Confocal μ-SRXRF: U and Pu intensity correlated

Characterisation of radioactive particles in the environment using advanced techniques
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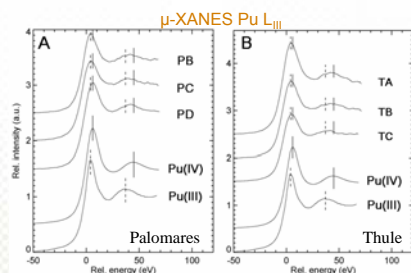
SEMIPALATINSK PARTICLES

Confocal 3D μ-XRF (ANKA, Karlsruhe)



11 slices (X: 30 μm) × 2D ZY scans 61 (10 μm) × 46 (10 μm) LT 3-4 sec
beam size: 8 μm (Z) × 9 μm (X) × 25 μm (Y)
= 30866 voxel-spectra

PALOMARES AND THULE PARTICLES NUCLEAR WEAPON ACCIDENTS



- Predominately UO_2 with presence of U_3O_8
- Pu present as Pu(III)/Pu(IV), Pu(IV)/Pu(V) or a mixture of all three oxidation states



PALOMARES AND THULE PARTICLES: VERY SIMILAR NUCLEAR WEAPON ACCIDENTS

- Same source - similar accident and release scenarios
In both accidents:
 - B-52 carrying thermonuclear bombs
 - Crash after fire in planes
 - Bombs detonated conventionally, subsequent explosive fire
 - Enriched U and weapon grade Pu coexist (mixed oxides), but not homogeneously mixed (inclusions)
 - ICP-MS results: Low $^{239}\text{Pu}/^{235}\text{U}$ (0.62-0.78) and $^{240}\text{Pu}/^{239}\text{Pu}$ (0.055-0.061) atom ratios
 - Similar morphology (Electron Microscopy)
 - Very similar XANES profiles
 - But, residing in very different environmental compartments since late 1960s (semi-desert for Palomares vs benthic marine for Thule)
- Particle characteristics apparently more dependent on the source and the release scenario than the environmental conditions



CONCLUSIONS

- Following a severe nuclear event with releases of refractory elements, a major fraction of released radionuclides will most probably be associated with particles.
- Particle characteristics are source-related and release-scenario dependent.
- Uranium and Pu contained in particles formed during explosive fires involving nuclear weapons or nuclear detonations in PUNE devices co-existed in inclusions or in the particle matrix
- Characterisation of particles formed due to explosive fires involving nuclear weapons in the Palomares and Thule accidents revealed that:
 - the particles contained significant amounts of enriched U in addition to weapon grade Pu in the form of mixed oxides,
 - source term has been a more important factor influencing weathering than local environmental conditions
- In view of the highly correlated U/Pu relationship, it seems plausible that the weapons involved in the Palomares and Thule accidents were based on composite $^{235}\text{U} + ^{239}\text{Pu}$ material fissile cores



**THANK YOU FOR YOUR
ATTENTION!**





Radioactive tracers for oil reservoirs - concept, tracers and analysis

Hartvig, Sven K and Bjornstad, Tor

Institute for Energy Technology, Reservoir and Exploration Technology, P.O. Box 40, NO-2027 Kjeller, Norway

Gas and water are being injected into oil reservoirs to give pressure support, avoid subsidence of the formation and to enhance the recovery of oil. To keep track of the injected water and gas, tracers are added to the different injection wells so that preferential flow directions, communication pathways, sweep volumes and breakthrough times can be calculated. Tracer technology can provide data about channelling and thief zones, large scale heterogeneities and sweep efficiencies that are almost impossible to get using other techniques.

Radioactive compounds such as tritiated water, tritiated alcohols, $^{22}\text{Na}^+$, $^{36}\text{Cl}^-$ and ^{14}C labelled thiocyanate are used for water tracing, while tritiated or ^{14}C labelled hydrocarbons are used for gas tracing.

Due to the very large dilution volumes in the reservoirs, sensitive techniques must be utilized for the detection of the tracers in the produced water and gas. The β -emitting tracers are analysed using Quantulus Ultra Low Level Liquid Scintillation Spectrometer® after removal of natural radioactivity and compounds that would cause quenching. Detection limits as low as 2 Bq/l of produced water for HTO and 5 mBq/L of produced gas for tritiated methane can be achieved.

Name	Sven Kristian Hartvig
Company / University	Institute for Energy Technology
Web-page	www.ife.no
Phone (direct line)	+47 63 80 61 47
Fax	+47 63 81 11 68
E-mail	Sven.Hartvig@ife.no

Radioactive Tracers for Oil Reservoirs — Concept, tracers and analysis

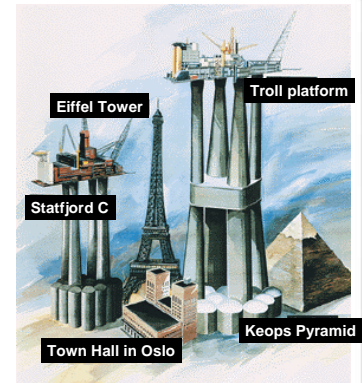


Sven K Hartvig and Tør Bjørnstad
Institute for Energy Technology (IFE)
Kjeller, Norway

15.01.2007



Size comparison of different well-known constructions

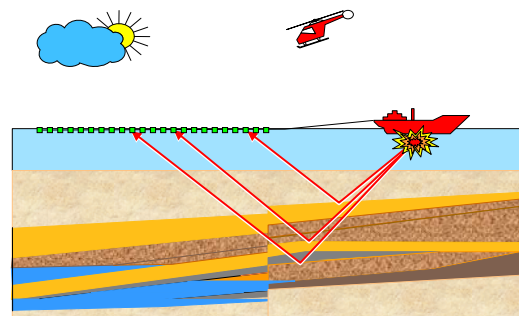


Outline

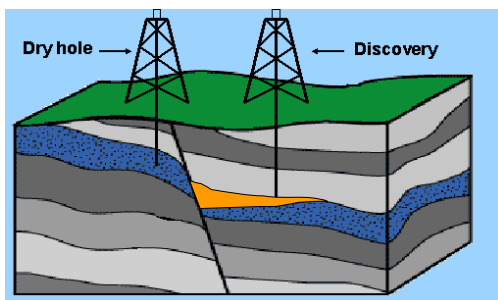
- Basics for oil exploration and production
- Qualification of tracers for reservoirs
- Analysis of samples
- Results from field experiments



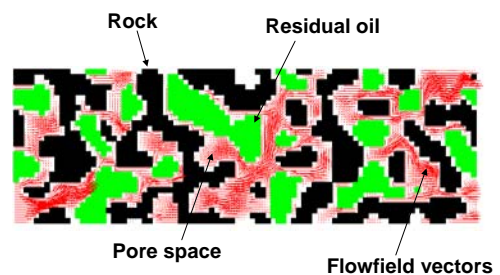
3D seismic examination



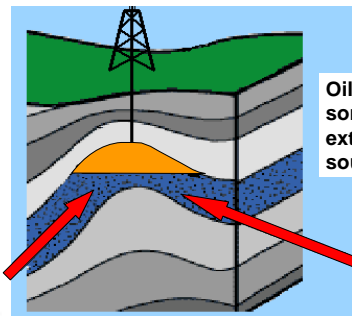
Exploratory drilling



Residual oil in water-wet rock



Oil & gas production

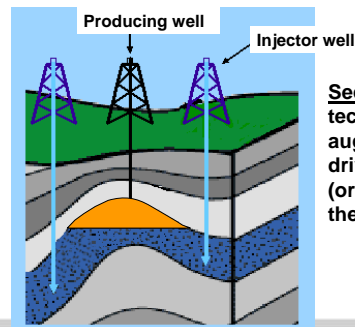


Oil production requires some type of "drive" to extract the oil from the source rock

1. Water Drive

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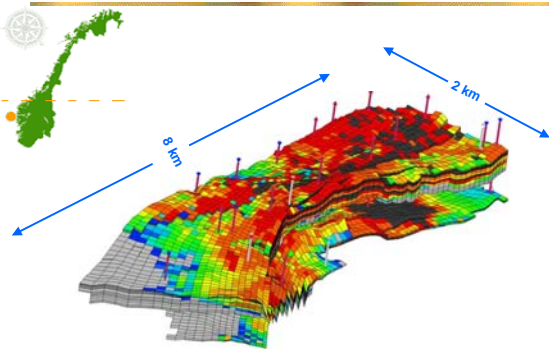
Enhanced recovery



Secondary recovery techniques involve augmenting the natural drive by injecting water (or gas) at the edges of the field.

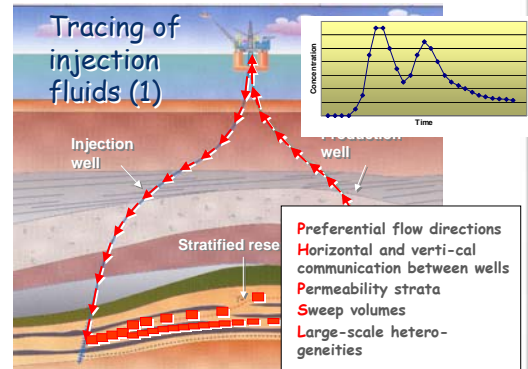
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Water expels oil



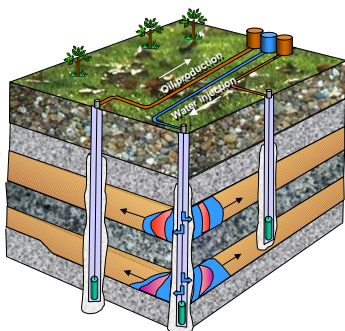
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Tracing of injection fluids (1)



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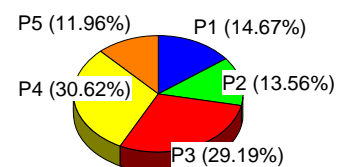
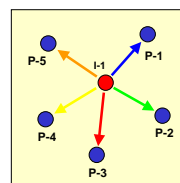
Water injection



IFE

Efficiency of water injection

Fraction of detected tracer



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Tracer types

It is found practical to divide available interwell tracers into three types based on their principally different production, treatment and analysis:

- Stable isotopic ratios (δD , $\delta^{13}C$...)
- Non-radioactive chemical species
- Radioactive atoms and molecules

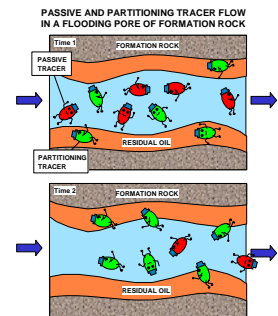


Behavior of interwell tracers

Two main tracer categories:

Passive tracers
(conservative, non-reacting)

Active tracers
(sorbing to rock, partitioning between liq. phases, reacting...)



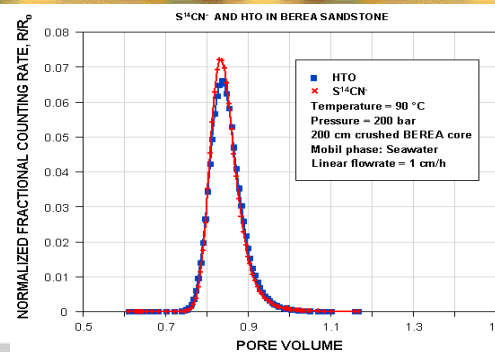
Passive-tracer requirements

Selection criteria for passive fluid tracers are:

- Insignificant degradation during the experiment
- Insignificant phase partitioning and sorption to rock
- Insignificant natural occurrence in reservoir fluids
- Detectable at very low concentrations
- Toxicity and radiotoxicity at an acceptable level
- Non-problematic logistics and handling
- Sufficient commercial availability
- Acceptable cost



Qualification of tracers



Common interwell radiotracers

As conservative (passive) water tracers:

1. Tritiated water, HTO, $E_\beta = 18$ keV, $T_{1/2} = 12.32$ y
2. $S^{14}CN^-$, $E_\beta = 159$ keV, $T_{1/2} = 5730$ y
3. Tritiated methanol, T-MeOH, $E_\beta = 18$ keV, $T_{1/2} = 12.32$ y
4. $^{60}Co(CN)_6^{3-}$, $E_\gamma = 1173$ and 1332 keV, $T_{1/2} = 5.2$ y
5. $^{22}Na^+$, $E_\gamma = 511$ and 1274 keV, $T_{1/2} = 2.5$ y

As oil/water partitioning tracers:

1. n-butanol, ^{14}C / 3H -labelled
2. IsoPropyl Alcohol, ^{14}C / 3H -labelled

As gas tracers:

1. 3H – labelled methane
2. 3H – labelled ethane



LSC in Tracer-technology

• TRACERS:

- HTO (tritiated water)
- $S^{14}CN^-$ (Carbon 14-labelled thiocyanat)
- CH_3T/C_2H_5T (tritiated methane/ethane)



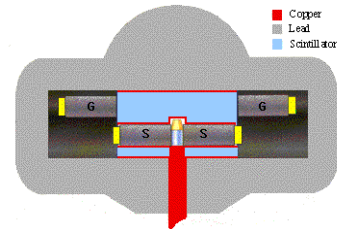
1220 QUANTULUS

The ultra low level liquid scintillation spectrometer from Wallac



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Quantulus detector and active guard

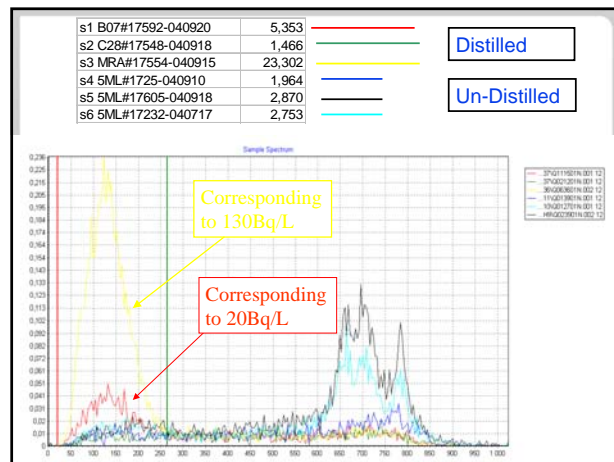


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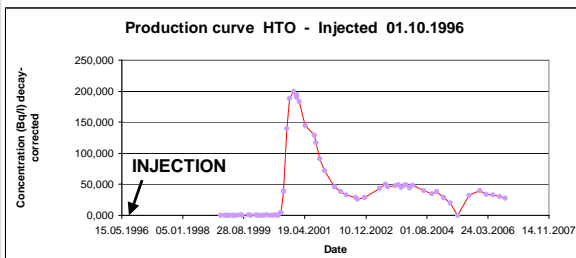
Analysis of HTO

- Produced water from oil-reservoirs, is filtered to remove oil and is then distilled to remove natural radioactivity
- 8 ml of the distilled water is mixed with 12ml of Scintillation cocktail (Ultima Gold, Low-Level Tritium, from Packard) in a PET vial and counted for 2 * 4 hours
- Background counting rate : 1,6-1,8 cpm (tritium window)
- Counting efficiency: 30-32 %, calculated for each sample from external standard quench correction method
- Detection limit : 1,5-2,0 Bq/l

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Production curve of HTO



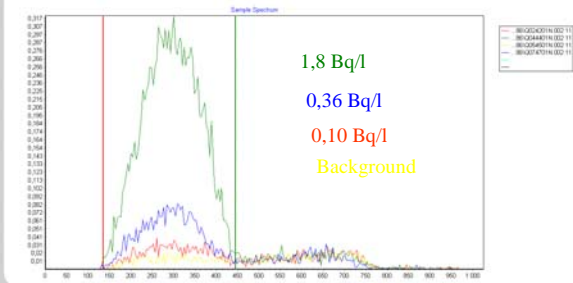
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Analysis of $S^{14}CN^-$

- Sample is filtered and then concentrated (a factor of 100) on anion-exchange column. The eluate (8 ml), containing concentrated $NaClO_4$, is mixed with 12ml of scintillation cocktail and counted using the Quantulus.
- Scintillation cocktail: Optiphase Supermix, Wallac.
- Counting Efficiency: 55-65 %, calculated for each sample from external standard quench correction method
- Background counting rate : ~3,5 cpm (^{14}C window)
- Detection limit: 0,01 Bq/l sample (1 Bq/l in eluate)

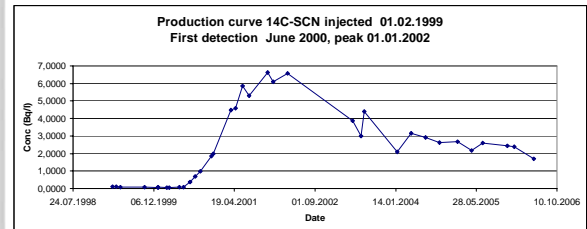
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Spectra of concentrated S¹⁴CN samples



IFE

Production curve S¹⁴CN



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Tritiated gas-tracers

- The tritiated methane or ethane is synthesised at IFE. Produced reservoir-gas is combusted and the water-vapour is condensed in a cooler
- Reaction: $\text{CH}_3\text{T} + 2\text{O}_2 \Rightarrow \text{CO}_2 (\uparrow) + \text{H}_2\text{O} + \text{HTO}$
- The HTO-content of the collected water is measured using the Quantulus
- Analytical conditions equal to the HTO-analysis
- Gas tracer detection limit: 5mBq/L gas

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Conclusions

- Tracing of injected water and gas
 - increase the understanding of the reservoirs
 - Leads to enhanced oil recovery
 - Reduces the amount of produced water
- β -active tracers can be detected in extremely low concentrations, adequate for the large dilution volumes in the reservoirs

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Evaluation of degree of readsorption of radionuclides during sequential extraction in soil: comparison between batch and dynamic extraction systems

Roongrat Petersen, Elo Harald Hansen and Xiaolin Hou

Department of Chemistry, Technical University of Denmark, Building 207, Kemitorvet, 2800 Kgs.-Lyngby, Denmark

Radiation Research Department, NUK-202, Risø National Laboratory, Frederiksborgvej 399, P.O. 49, DK-4000 Roskilde

Sequential extraction techniques have been widely used to fractionate metals in solid samples (soils, sediments, solid wastes, etc.) due to their leachability. The results are useful for obtaining information about bioavailability, potential mobility and transport of element in natural environments. However, the techniques have an important problem with redistribution as a result of readsorption of dissolved analytes onto the remaining solids phases during extraction. Many authors have demonstrated the readsorption problem and inaccuracy from it.

In our previous work, a dynamic extraction system developed in our laboratory for heavy metal fractionation has shown the reduction of readsorption problem in comparison with the batch techniques. Moreover, the system shows many advantages over the batch system such as speed of extraction, simple procedure, fully automatic, less risk of contamination and less dependency on extraction conditions. Therefore, it is thought that the dynamic extraction system would show less readsorption problem for radionuclides.

This work emphasizes on the study of readsorption of Pu and Am when both batch and dynamic extraction systems are employed. For the dynamic extraction procedure, an extraction column (cylindrical shape, volume ca. 3 mL) is designed and implemented into the conduit of sequential injection setup. The sample is filled in the extraction column and different extracting reagents are pumped sequentially through the column by mean of the syringe pump. In this study, a method of standard addition into extractants was used to evaluate readsorption phenomena in the modified standard, measurement and testing programme's (SM&T) sequential extraction scheme.

The result showed that the dynamic extraction system gave similar degree of readsorption for both Pu and Am compared with the batch system. Step-wise tests indicated that 80% of Pu and over 90% of Am extracted from exchangeable fraction was readsorbed. And over 95% of Pu and Am from acid soluble and reducible fractions were readsorbed. Pu and Am mainly readsorbed to oxidizable fraction or organic matter phase even at low organic content (2.5 wt.%).

Name	Roongrat Petersen
Company / University	Department of Chemistry, Technical University of Denmark, Building 207, Kemitorvet, 2800 Kgs.-Lyngby, Denmark
Web-page	www.kemi.dtu.dk
Phone (direct line)	+45 4525 2357
Fax	+45 4588 3136
E-mail	toey@kemi.dtu.dk

Chemical Fractionation of Pu and Am in Soils and Sediments

Readsorption Study

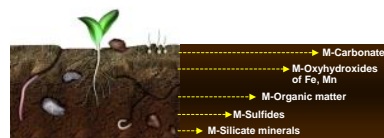
Roongrat Petersen

Technical University of Denmark (DTU)

In collaboration with Radiation Research Department, Risø

Why Chemical Fractionation in Soils and Sediments?

- Metals bound to different phases in soil samples with different mechanisms
- They are different in leachability / mobility to the environment



- Soil Fractionation
IUPAC: Distribution of elements in the solid phase

Soil Extraction (Operationally defined speciation) Started in the early 1970s

Operationally-defined fraction	Extractant
Exchangeable	CaCl_2 , MgCl_2 , BaCl_2
Acid soluble (Carbonate)	HOAc , NaOAc
Easily reducible (Mn oxide)	$\text{NH}_2\text{OH}\cdot\text{HCl}$
Easily oxidisable (Humic and fulvic acids)	$\text{K}_2\text{P}_2\text{O}_7$, NaOCl
Moderately reducible (Amorphous Fe oxide)	$\text{NH}_2\text{OH}\cdot\text{HCl}/\text{HOAc}$, $\text{NH}_2\text{Ox}/\text{HOx}$
Oxidisable (Oxides+sulphide)	H_2O_2 , $\text{H}_2\text{O}_2/\text{NH}_4\text{OAc}$
Residual	HF , $\text{HF}+\text{HNO}_3$

Metal mobility ↑

How to perform soil extraction? Batch Sequential Extraction



3

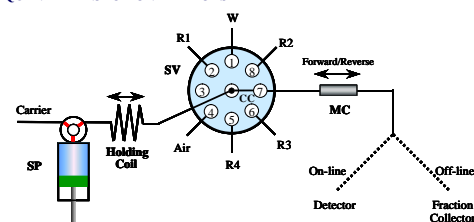
Batch Sequential Extractions

LIMITATIONS:

- ✓ Lengthy and tedious procedures (4-5 days)
- ✓ Risk of sample contamination due to manipulation
- ✓ Non-selectivity of reagents (phase overlapping)
- ✓ Readsorption and redistribution of extracted compounds
- ✓ Lack of automation
- ✓ No information on the kinetics of the leaching (equilibrium based)
- ✓ Impossibility of mimicking dynamic environmental conditions

Flow-through dynamic extractions (Previous work -stable elements)

SEQUENTIAL INJECTION METHODS

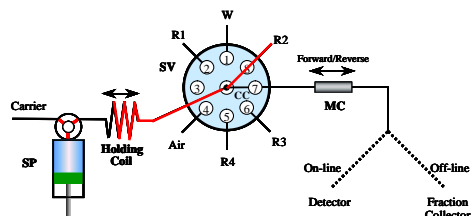


- Fully automated, programmable and enclosed system
- Selection of extractant volumes and flow rates at will
- Can mimic the real environments better than the batch system
- Offer a versatile mode of operation

Analytical Chemistry 77 (2005) 2720-2726
 Analytica Chimica Acta 536 (2005) 183-190
 Analytica Chimica Acta 526 (2004) 177-184
 Trends in Analytical Chemistry 24 (2005) 759-771

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SEQUENTIAL INJECTION METHODS

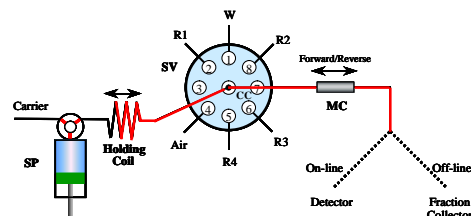


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 Trends in Analytical Chemistry 24 (2005) 759-771

Flow-through dynamic extractions (Previous work -stable elements)

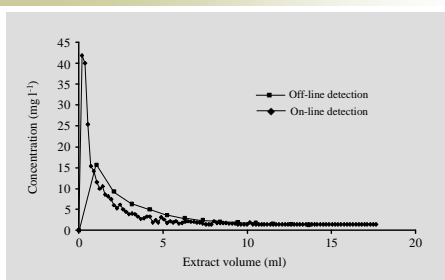
SEQUENTIAL INJECTION METHODS



- Fully automated, programmable and enclosed system
- Selection of extractant volumes and flow rates at will
- Can mimic the real environments better than the batch system
- Offer a versatile mode of operation

Analytical Chemistry 77 (2005) 2720-2726
 Analytica Chimica Acta 536 (2005) 183-190
 Analytica Chimica Acta 536 (2004) 177-184
 Trends in Analytical Chemistry 24 (2005) 759-771

Dynamic extraction with on-line and off-line FAAS detection

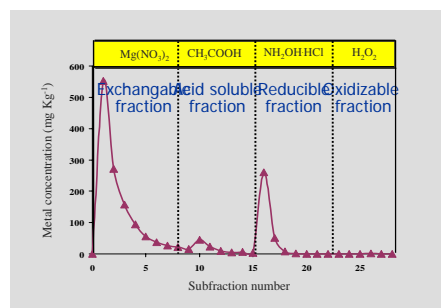


Extractograms for Cu with EDTA extraction, comparing the concentration of Cu in each subfraction;
 Off-line, 1.0 mL per subfraction; on-line, 175 µL per injection; sample, CRM483 (300 mg).

Analytical Chemistry 77 (2005) 2720-2726

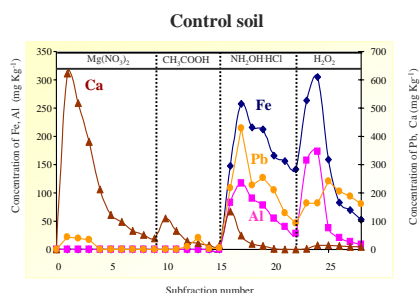
Distribution of metal in soil

(predict the mobility of metal in soil to the environment)



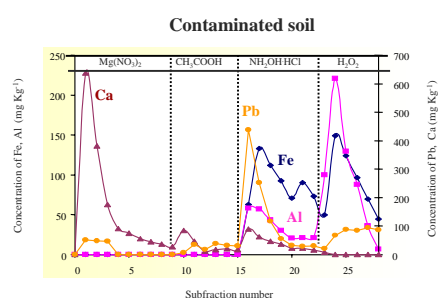
Association of metals in soil

(predict source and occurrence of metal in soil sample)



Association of metals in soil

(predict source and occurrence of metal in soil sample)



Chemical Fractionation of Pu and Am in Soils and Sediments

Analytical Solutions to Current Problems



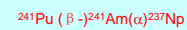
January 1968 : an american bomber carrying 4 Plutonium-bearing weapons crashed on the sea ice in Bylot Sound, 11 km west of the Thule Air Base.

Released of kilogram quantities of Pu

Pu investigation : Thule Air Base

Since 1969, a numbers of expeditions have been organized by Risø to investigate the inventory of Pu, its distribution and dispersion in the accident area (1969, 1971, 1974, 1980, 1988, 2002).

No chemical speciation studies of Pu and its decay products (^{237}Np , ^{241}Am)



It is very important to predict of the **fate** of these radionuclides and accurate **risk assessment** of the radiation

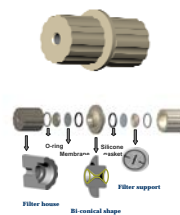


Aims of the research

- To develop a dynamic sequential extraction technique for fractionation of Pu, Am in soils and sediments

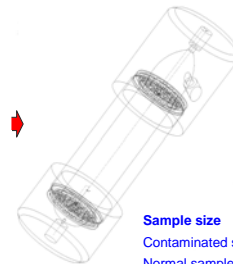
Extraction column for dynamic sequential extraction

Previous work



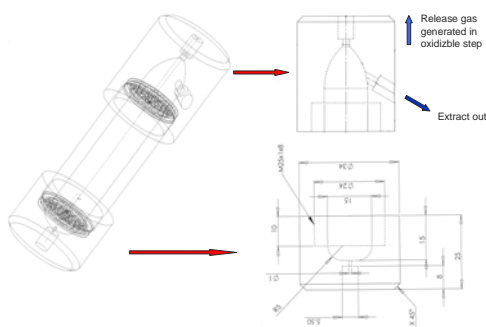
Microcolumn ca. 400 μL
Max 300 mg soil

This work



Sample size
Contaminated sample : ca. 0.5-1 g
Normal sample : up to 5 g
Extraction flow rate : 2 mL/min
Uniform flow rates are obtained.

Extraction column for dynamic sequential extraction



Aims of the research

- To develop a dynamic sequential extraction technique for fractionation of Pu, Am in soils and sediments
- To investigate the readsorption/redistribution problem of radionuclides in the developed methods

Readsorption/redistribution problem during sequential extraction

What is readsorption?

Readsorption and redistribution

Trace metals released by one extractant could associate again with other undissolved solid components within the time-scale of the extraction step

Readsorption problem

Dissolving phase → underestimated
Receiving phase → overestimated

Readsorption/redistribution problem during sequential extraction

Compare degree of readsorption between batch and dynamic sequential extraction method

Method of readsorption study

- Model soils containing single and mixed synthetic phases
- Natural soils spiked with pure synthetic phases
- Standard addition in the extractant method

Standard addition in the extractant method

²⁴²Pu and ²³⁸Pu
²⁴³Am and ²⁴⁴Cm

It is thought that dynamic systems would have less readsorption problem

Readsorption/redistribution problem during sequential extraction

Table 1 Summary of %recovery of spiked Pu in extracting reagents for each step by a dynamic system as compared to a conventional batch system

Readsorption study in Step	System	Replicate	Spiked Pu-242 (Bq)	Pu-242 extracted with unspiked extractant (Bq)	Pu-242 extracted with spiked extractant (Bq)	% Recovery of spiked Pu-242	% Readsorption of Pu-242
I. Exchangeable phase	Batch	1	0.2015	ND	0.0469	24	76
		2	0.2008	ND	0.0430	21	79
	Flow	1	0.2005	ND	0.0580	29	71
		2	0.2064	ND	0.0472	23	77
II. Acid soluble phase	Batch	1	0.2017	ND	0.0075	3.7	96
		2	0.2021	ND	0.0056	2.8	97
	Flow	1	0.2011	ND	0.0086	4.3	96
		2	0.2540	ND	0.0080	3.9	96
III. Reducible phase	Batch	1	0.1999	ND	0.0013	0.6	99
		2	0.1993	ND	0.0017	0.8	99
	Flow	1	0.1997	ND	0.0033	1.7	98
		2		ND			

Sample: soil from Tystofte 3 g in all cases
ND: not detectable

Readsorption/redistribution problem during sequential extraction

Table 2 Summary of %recovery of spiked Am in extracting reagents for each step by a dynamic system as compared to a conventional batch system

Readsorption study in Step	System	Replicate	Spiked Am-243 (Bq)	Am-243 extracted with unspiked extractant (Bq)	Am-243 extracted with spiked extractant (Bq)	% Recovery of spiked Am-243	% Readsorption of Am-243
I. Exchangeable phase	Batch	1	0.2006	ND	0.0156	7.8	92
		2	0.2011	ND	0.0195	10	90
	Flow	1	0.2006	ND	0.0049	2.4	98
		2		ND			
II. Acid soluble phase	Batch	1	0.1994	ND	0.0031	1.6	98
		2	0.2023	ND	0.0026	1.3	99
	Flow	1	0.1991	ND	0.0016	0.8	99
		2		ND			
III. Reducible phase	Batch	1	0.2010	ND	0.0148	7.4	93
		2	0.2003	ND	0.0018	0.9	99
	Flow	1	0.1990	ND	0.0060	3.0	97
		2		ND			

Sample: soil from Tystofte 3 g in all cases
ND: not detectable

Readsorption/redistribution problem during sequential extraction

Table 3 Percent recovery of spiked Pu-242

Spiked Pu-242 in step	System	Replicate	Spiked Pu-242 (Bq)	%Recovery (Bq)						Total (I+II+III+IV+V)
				Step I* (Exchangeable)	Step II* (Acid soluble)	Step III* (Reducible)	Step IV* (Oxidizable)	Step V* (Residue)		
I	Batch	1	0.2015	24 (0.0469)	0.1 (0.0023)	0.3 (0.0006)	37 (0.0740)	0.6 (0.0012)	62 (0.1250)	
		2	0.2008	21 (0.0430)	0.5 (0.0010)	0.3 (0.0007)	46 (0.0930)	0.2 (0.0005)	68 (0.1382)	
	Flow	1	0.2005	29 (0.0580)	1.0 (0.0016)	0.5 (0.0006)	60 (0.1170)	6.0 (0.0117)	96 (0.1889)	
		2	0.2064	23 (0.0472)	1.0 (0.0021)	0.4 (0.0008)		24 (0.0491)		
II	Batch	1	0.2017	ND	3.7 (0.0075)	0.3 (0.0007)	70 (0.1419)	0.3 (0.0007)	74 (0.1508)	
		2	0.2021	ND	2.8 (0.0056)	0.2 (0.0005)	65 (0.1321)	0.3 (0.0007)	68 (0.1389)	
	Flow	1	0.2011	ND	4.3 (0.0086)	0.5 (0.0010)	8.6 (0.0174)	1.4 (0.0028)	15 (0.0298)	
		2	0.2054	ND	3.9 (0.0080)	0.5 (0.0010)	65 (0.1340)	3.7 (0.0076)	73 (0.1506)	
III	Batch	1	0.1999	ND	ND	0.6 (0.0013)	66 (0.1342)	0.4 (0.0008)	67 (0.1363)	
		2	0.1993	ND	ND	0.8 (0.0017)	62 (0.1256)	1.1 (0.0022)	64 (0.1295)	
	Flow	1	0.1997	ND	ND	1.7 (0.0033)	45 (0.0912)	40 (0.0831)	87 (0.1776)	
		2		ND	ND					

Sample: soil from Tystofte 3 g in all cases, ND=Not detectable
* Original Pu-242 concentrations in soil in each step are less than detection limit.

Lanthanide added-Can solve the problem?

Table 4 Percent recovery of spiked Pu in extracting reagent for acid soluble step (step II) plus adding lanthanide elements as competing elements by batch extraction method (n=1)

Lanthanide elements	Spiked concentration (ppm)	Spiked Pu-242 (Bq)	Pu-242 extracted with unspiked extractant (Bq)	Pu-242 extracted with spiked extractant (Bq)	% Recovery of spiked Pu-242	% Readsorption of Pu-242
La	2	0.2098	ND	0.0032	1.5	99
	20	0.2083	ND	0.0033	1.6	98
Gd	2	0.2092	ND	0.0046	2.2	98
	20	0.2101	ND	0.0028	1.3	99
Pr	2	0.2099	ND	0.0038	1.8	98
	20	0.2105	ND	0.0029	1.4	99
Nd	20	0.2076	ND	0.0033	1.6	98
Eu	20	0.2118	ND	0.0035	1.7	98

Sample: soil from Tystofte 3 g in all cases
ND = Not detectable

Readsorption/redistribution problem during sequential extraction

- Extracted Pu trends to readsorb mainly to organic matter phase even though the selected sample contains low organic matter (2%).
- In order to have less readsorption, organic matter phase has to be extracted at the beginning of sequential extraction.
- Complexing agents can be used as hold-back reagents to lessen the effect of readsorption but further investigation is needed.

Readsorption/redistribution problem during sequential extraction

Eventhough dynamic extraction cannot solve the readsorption problem
But the system is still very promising because

- The dynamic extraction system is a closed system, no sample loss, less risk of personal errors and contamination. Therefore it gives higher recoveries (ca. 67% recovery by batch and ca. 85% by dynamic)
- Almost continuous extraction can be performed which can better mimic the real environments
- The system is automated and controlled by computer and offers a versatile mode of operation
- Extraction time for 4 steps extraction is totally 8 h compared to ca. 50 h (without separation procedure by centrifuge and filtration) in batch systems
- A more detailed knowledge of the leaching kinetics can be obtained in comparison with the batch system

Acknowledgements

- * Hans Christian Ørsted Postdoc Programme, DTU
- * Analytical and Bioinorganic Chemistry group, DTU
- * Radioecology Programme (RAS),
Radiation Research Department, Risø

Thank you for your attention



Time series and correlations in ^{137}Cs concentrations in the fish fauna of the lake Apukkajärvi in Finnish Lapland

Jarkko Ylipieti and Dina Solatie

STUK Radiation and Nuclear Safety Authority (Regional laboratory in Northern Finland)

The radioactive fallout in Finnish Lapland from the nuclear reactor accident in Chernobyl in 1986 was low, for ^{137}Cs in average 1000 Bq/m². The enrichment of radionuclides in the special food chain like lake water - fish - man is however very effective.

Lake Apukkajärvi is situated in the Northern Finland near by the Arctic Circle. The lake is small, low and highly eutrophic. The fish fauna consist of pike, perch, burbot and roach. From year 1982 to 2006 the Radiation and Nuclear Safety Authority's Regional Laboratory of Northern Finland has caught fishes in the lake. All samples have been collected with traps, which have been emptied twice a week in a summer time (June-July-August). In this study pike, perch and roach ^{137}Cs concentrations have been analysed by gamma spectrometry and the results of the measurements have been processed statistically.

The aim of this study was to find out trends in time series and correlations in measured parameters of the samples. Trends are important indicators to help to understand the ecology of the lake and correlations give information, which are needed to see the relationships between two or more parameters.

Name	Jarkko Ylipieti
Company / University	Radiation and Nuclear Safety Authority (Regional laboratory in Northern Finland)
Web-page	http://www.stuk.fi/tutkimus/units/en_GB/northern_finland/
Phone (direct line)	+358 16 1814482
Fax	+358 16 3794369
E-mail	jarkko.ylipieti@stuk.fi

Trends and Correlations in ^{137}Cs Concentrations in the Fish Fauna of the Lake Apukkajärvi in Finnish Lapland

*Jarkko Ylipietä and Dina Solatie STUK-Radiation and Nuclear Safety Authority,
Regional Laboratory in Northern Finland, 96500 Rovaniemi, Finland*

Abstract

The radioactive fallout in Finnish Lapland from the nuclear reactor accident in Chernobyl in 1986 was low, for ^{137}Cs in average 1000 Bq/m². The enrichment of radionuclides in the special food chain like lake water - fish - man is however very effective. Lake Apukkajärvi is situated in the Northern Finland near by the Arctic Circle. The lake is small, low and highly eutrophic. The fish fauna consist of pike, perch, roach and burbot. From year 1982 to 2006 the Radiation and Nuclear Safety Authority's Regional Laboratory of Northern Finland has caught fish in the lake.

The aim of this study was to find out trends and correlations in measured parameters of the samples. Trends are important indicators to help to understand the ecology of the lake and correlations give information, which are needed to see the relationships between two or more parameters.

Materials and Methods

All samples were collected with traps, which were emptied twice a week in a summer time (June-July-August). In this study ^{137}Cs concentrations in pike, perch and roach were analysed by gamma spectrometry and the results of the measurements were processed statistically.

Results

Number of the samples, deviations and averages of the ^{137}Cs concentrations in perch, pike and roach meat are presented in table 1.

Table 1. Statistical numbers divided to different time series.

	perch	pike	roach
period 1			
n	30	28	12
dev	21-151	26-150	10-39
avg	55	72	22
period 2			
n	100	70	26
dev	9-65	13-70	5-17
avg	25	32	12

Calculated averages per year ^{137}Cs concentrations [Bq/kg f.w] are illustrated in scatter plots in logarithmic scale as a function of time (Fig 2.1, 2.2, 2.3). Time series are divided in to two periods; years after Chernobyl accident 1986 to year 1994 and the second from 1995 to 2006. Finally observations of the time series were approximated to straight line and with the given equation ecological half lives were estimated to each class.



Fig 1. Location of the Lake Apukkajärvi

Discussion and Conclusions

After the Chernobyl accident in the late spring in 1986 ^{137}Cs concentrations increased rapidly in the flesh of perch and pike. Although they were not high in the same summer, but next year ^{137}Cs concentrations were ten times higher than before the accident. The speed of decrease in ^{137}Cs concentrations were fast in the first eight years and then it has seemed to slow down significantly (Fig 2.1, 2.2, 2.3).

Estimated ecological half-lives in years [a] for perch, pike and roach are presented in each plot.



Fig 2.1 Perch
1st period 3,7a
2nd period 21,3a

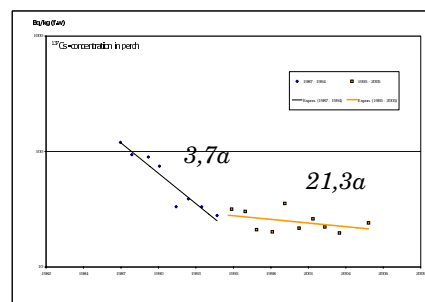


Fig 2.2 Pike
1st period 6,5a
2nd period 28,8a

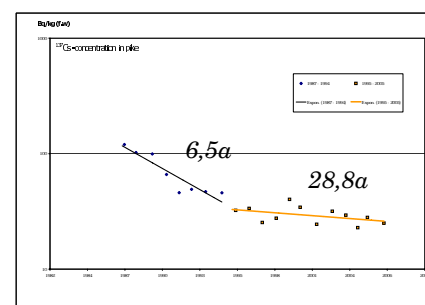
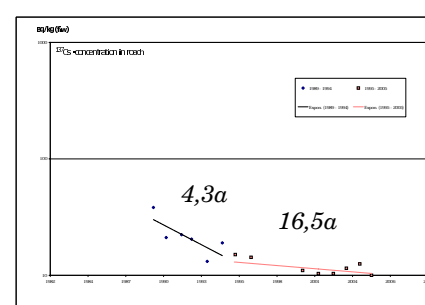


Fig 2.3 Roach
1st period 4,3a
2nd period 16,5



Correlations between fish and the lake water were not analysed in this study, because of the incoherence of the fresh water data. Further studies are needed to get information about the transfer factors in the foodchain water - fish - man.



Soluble and particle bound ^{238}U -series radionuclides in ground waters

Kaisa Vaaramaa and Jukka Lehto

Laboratory of Radiochemistry, P. Box 55, 00014 University of Helsinki, Finland

Appreciable concentrations of natural uranium and its daughter radionuclides may occur in drinking water obtained from drilled wells. About 300,000 people in Finland permanently use water from drilled wells. Elevated concentrations of natural radionuclides in drinking water can cause unacceptable radiation doses to the consumers. Therefore, the waters should be purified before use. The aim of the study was to determine whether uranium, ^{226}Ra and ^{210}Po and ^{210}Pb are present in drilled well waters in ionic form and so might be removed with ion exchangers [1].

Water of five drilled wells was filtered with three membranes (pore size 0.45 μm , 50 nm and 5 kD) to determine the soluble and particle-bound forms of $^{234,238}\text{U}$, ^{226}Ra and ^{210}Po . Three of the waters were of CaHCO_3 type and two of NaCl type. Some of the waters also have high concentrations of Fe, Mn and humic substances. $^{234,238}\text{U}$ was present entirely in soluble form in all waters, probably as uranyl ion complexed with carbonate. Radium was mainly in soluble form, but 10% of the total ^{226}Ra activity was bound to particles in the Fe-Mn-rich waters. The behaviour of polonium is complex in natural waters; ^{210}Po was present in both soluble and particle-bound forms in all the ground waters. A correlation was observed between the fractions of particle-bound ^{210}Po and the concentrations of iron in raw waters.

Uranium and radium were almost completely in ionic form and ion exchange is an effective method for removal these radionuclides from drinking water. Polonium and ^{210}Pb [1] were present both soluble form and bound in particles. Thus ion exchange would remove part of the polonium and ^{210}Pb , but membrane filtration would also be required.

Reference

1. Vaaramaa, K., Physico-Chemical Forms of Natural Radionuclides in Drilled Well Waters and Their Removal by Ion Exchange, Doctoral Thesis, University of Helsinki, Department of Chemistry, Laboratory of Radiochemistry, 2003 (<http://ethesis.helsinki.fi>)

Name	Kaisa Vaaramaa
Company / University	University of Helsinki
Web-page	http://www.helsinki.fi/kemia/radiokemia/english/
Phone (direct line)	+358 9 191 50162
Fax	+358 9 191 50121
E-mail	Kaisa.Vaaramaa@helsinki.fi

Soluble and particle-bound ^{238}U -series radionuclides in ground waters

About 300,000 people in Finland permanently use water from drilled wells. The use of the granitic bedrock water can cause unacceptable radiation doses to the consumers and therefore the removal of natural radionuclides is necessary. The aim of the study was to determine whether uranium, ^{226}Ra and ^{210}Po and ^{210}Pb are present in drilled well waters in ionic form and so might be removed with ion exchangers.¹

Materials and methods

Ground water samples

- from five drilled wells
- waters had been used as a source of drinking water
- high concentrations of natural radionuclides (^{238}U , ^{226}Ra , ^{210}Po up to 923 $\mu\text{g/l}$, 23 Bq/l, 7 Bq/l, respectively)
- Ca-HCO₃ type waters (water 1, 2, and 3) and Na-Cl type waters (water 4 and 5). Waters 3, 4 and 5 had high Fe, Mn and organic matter concentrations.

Filtration of ground waters

- Sartorius Ultrasart® Cell 50 ml pressure filtration system with a stirrer
- 250 ml sample
- Gelman Laboratory polyethersulfone filters (Ø47 mm): 450 nm, 50 nm, 5 kD (~ 1 nm in pore size)
- overpressure 0.5–2 bar
- two parallel determinations

Determination of the radioactivities

- ^{226}Ra from its daughter, ^{214}Po , with a low background scintillation counter Quantulus™ (Wallac)
- ^{210}Po and $^{234,238}\text{U}$ by alpha spectrometric methods

Figure 1. Distribution of ^{210}Po activity (%) in different particle-size fractions in ground waters. The fraction of ^{210}Po adsorbed on the filtration system and filters is shown on the right side of the figure (adsorption).

Results

$^{234,238}\text{U}$ was in soluble form in the drilled well waters, i.e. all of the U activity passed through the 5 kD filter. Of the total ^{226}Ra activity, 10% was bound on particles in Fe–Mn-rich waters. ^{210}Po was present in both soluble and particle-bound forms in all the ground waters (Fig. 1 and Table 1). A correlation was observed between the fractions of particle-bound ^{210}Po and the concentrations of iron in raw waters.

Table 1. Fractions of ^{210}Po in soluble form in the ground waters.

Water	Fe tot. (mg/l)	Mn (mg/l)	Soluble ^{210}Po (%)*
1	0.011	0.015	67.9 ± 8.92
2	0.018	0.011	43.4 ± 4.82
3	1.05	1.12	32.4 ± 2.68
4	1.1	0.25	4.86 ± 0.34
5	1.8	0.85	7.54 ± 0.64

*Soluble ^{210}Po i.e. fraction left after 5 kD filter.

Conclusions

Uranium and radium were almost completely in ionic form and ion exchange is an effective method for removal these radionuclides from drinking water. ^{210}Po and ^{210}Pb were present both in soluble form and bound in particles. Thus ion exchange would remove part of the polonium and ^{210}Pb , but membrane filtration would also be required.

Reference

1. Vaaramaa, K., *Physico-Chemical Forms of Natural Radionuclides in Drilled Well Waters and Their Removal by Ion Exchange*, Doctoral Thesis, University of Helsinki, Department of Chemistry, Laboratory of Radiochemistry, 2003 (<http://ethesis.helsinki.fi>).



Detection of irradiated foods by the thermoluminescence of mineral contamination

M.H. Palosaari

Laboratory of Radiochemistry, Department of Chemistry, University of Helsinki, P.O. Box 55, FIN-00014 University of Helsinki, Finland

The irradiation of foods, except for spices and sterile diets for hospital use, were prohibited in Finland under statute 844/87. A suitable method for identifying irradiated foods was developed in the laboratory of Radiochemistry at the University of Helsinki during years 1988-1990.1 This method is based on measuring the thermoluminescence (TL) of mineral contaminants in food and the official European procedure can be found in the CEN (European Committee for Standardization) standard EN1788.

The minerals are normally separated from the sample with CCl_4 or flushing the samples with water. The minerals are freed from organic material with high density liquid sodium polytungstate and isolated minerals are rinsed with water and dried with acetone. The TL of the separated minerals are measured with Risø TL-DA-10 instrument with a blue Corning 7-59 filter and a glow curve -data is recorded. The measured minerals are irradiated with a ^{60}Co source to a dose of 1 kGy and measured again for a second glow curve. The TL intensities of the glow curves are integrated over temperature range 200 °C to 250 °C and the curves are compared. If the glow curve ratio is 0.1 or under, the sample is not irradiated and if the glow curve ratio is over 0.5, the sample is irradiated. Between glow curve ratio 0.1-0.5 the identification of irradiation is based on the shapes of the curves.

This method of TL analysis has been used for the official control of irradiated foods in Finland since 1990.

REFERENCES

1. Autio T. and Pinnioja S., 1990. Zeitschrift für Lebensmittel-Untersuchung und -Forschung 191, pp. 177-180.

Name	Miia H. Palosaari
Company / University	University of Helsinki
Web-page	http://www.helsinki.fi/kemia/radiokemia/
Phone (direct line)	+358 50 368 7016
E-mail	miia.h.palosaari@helsinki.fi

Detection of Irradiated Foods by the Thermoluminescence of Mineral Contamination

INTRODUCTION

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METHODS

The minerals are normally separated from the sample with CCl_4 or flushing the samples with water. The minerals are freed from organic material with high density liquid sodium polytungstate and isolated minerals are rinsed with water and dried with acetone. The TL of the separated minerals are measured with Risø TL-DA-10 instrument with a blue Corning 7-59 filter and a glow curve -data is recorded. The measured minerals are irradiated with a ^{60}Co source to a dose of 1 kGy and measured again for a second glow curve.

CONCLUSIONS

The TL intensities of the glow curves are integrated over temperature range 200 °C to 250 °C and the curves are compared. If the glow curve ratio is 0,1 or under, the sample is not irradiated (fig. 5) and if the glow curve ratio is over 0,5, the sample is irradiated (fig. 6). Between glow curve ratio 0,1-0,5 the identification of irradiation is based on the shapes of the curves (fig. 7).

This method of TL analysis has been used for the official control of irradiated foods in Finland since 1990.



Fig 1. Mineral separation with CCl_4 .



Fig 2. Isolated minerals in a platinum plate



Fig 3. TL-DA-10 instrument



Fig 4. ^{60}Co source

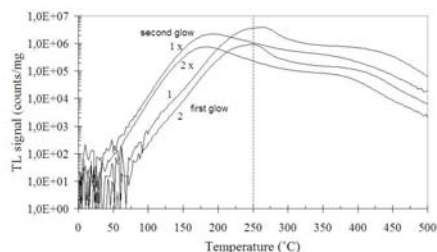


Fig 5. Glow ratio > 0,5

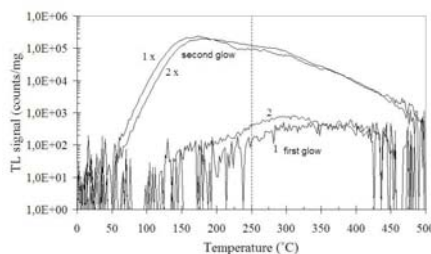


Fig 6. Glow ratio < 0,1

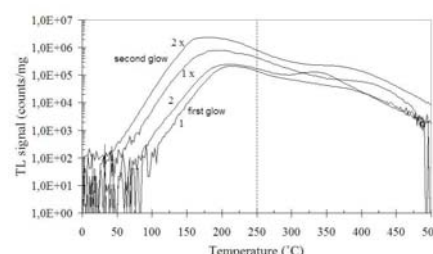


Fig 7. Glow ratio 0,1 - 0,5

REFERENCE

1. Autio T. and Pinnioja S., 1990. Zeitschrift für Lebensmittel-Untersuchung und -Forschung 191, pp. 177-180.



Practical course on radionuclide production

Lalli Jokelainen, Mervi Söderlund and Kerttuli Helariutta

Laboratory of Radiochemistry, Department of Chemistry,
University of Helsinki, P.O. Box 55, FIN-00014 University of Helsinki, Finland

Combining the teaching of radiochemistry with a real scientific research work both allows students to get a glimpse of professional possibilities after their graduation as well as to ties them as a part of scientific community already at early stage. In University of Helsinki, Department of Chemistry, Laboratory of Radiochemistry we have realised this twice, in years 2004 and 2006, organising a course "Practical course on radionuclide production".

The practical course on radionuclide production is meant for undergraduate and postgraduate students of radiochemistry. It is held every second autumn at the Laboratory of Radiochemistry in collaboration with the scientists from V.G Khlopin Radium Institute, St. Petersburg. During the course the different stages involved in preparing a radioactive tracer are covered. The course consists of lectures and practical laboratory work involving chemical separations and radiation measurements.

The practical part of the course starts with irradiation of a set of targets, using stack foil method. After 24 hours of irradiation and 24 hours of cooling the activity of the produced nuclides in targets is measured with alpha- and gamma detectors. The position of the beam spot is located with autoradiography and cut out. Chemical separation of different reaction products from target material is carried out according to the procedure described in an article by Horwitz et al. [1]. Fractions produced in chemical separations are first measured with a gamma detector and then prepared as alpha samples for alpha spectroscopy. For each produced tracer nuclide, precentual yield in each fraction is calculated and combined as total activity. The production cross sections of different nuclides are calculated from measured activities. The course is finalised by written reports by the students. The final results will be published in a scientific journal.

Practical working is probably the best way to learn and understand things. In this course the degree of learning is greatly dependent on the students own activity and interest because of the intensive nature of the course; chemical separations take up to twelve hours per target and the pace of work is hectic. Despite of being challenging and demanding, the comments from the students are that the course is very satisfying and rewarding, mostly because of the inspiring visiting lectures.

References:

- [1] Horwitz et al Separation and preconcentration of actinides from acidic media by extraction chromatography; Analytica Chimica Acta, Volume 281, Issue 2, 10 September 1993, Pages 361-372

Name	Lalli Jokelainen
Company / University	University of Helsinki
Web-page	http://www.helsinki.fi/kemia/radiokemia/
Phone (direct line)	+358 40 565 7971
E-mail	lalli.jokelainen@helsinki.fi

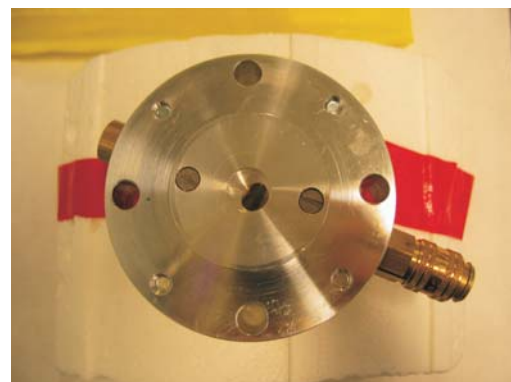


Practical course on isotope production

Mervi Söderlund, Lalli Jokelainen and Kerttuli Helariutta
Laboratory of Radiochemistry, Department of Chemistry, University of Helsinki, Finland

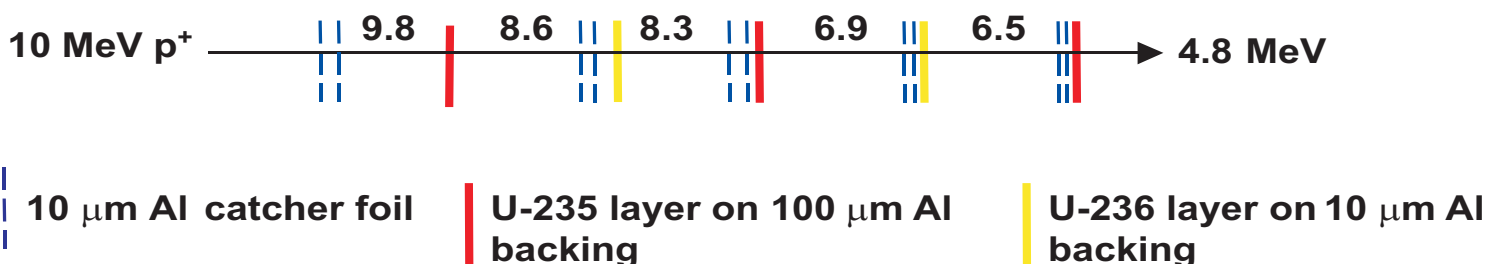
Introduction

The practical course on radionuclide production is meant for undergraduate and postgraduate students of radiochemistry. It is held every second autumn at the Laboratory of Radiochemistry in collaboration with the scientists from V.G. Khlopin Radium Institute, St. Petersburg. During the course the different stages involved in preparing a radioactive tracer are covered. The course consists of lectures and practical laboratory work involving chemical separations and radiation measurements.



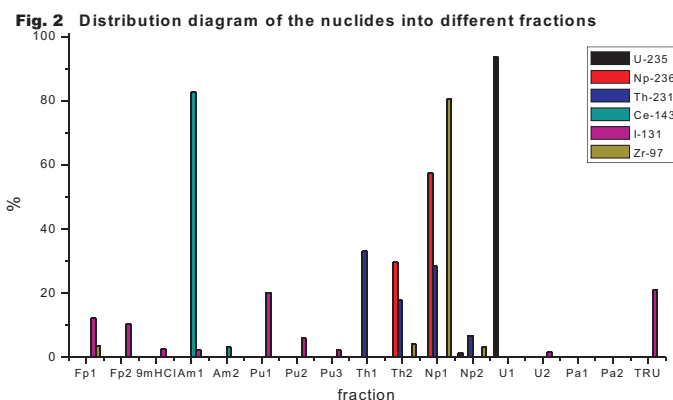
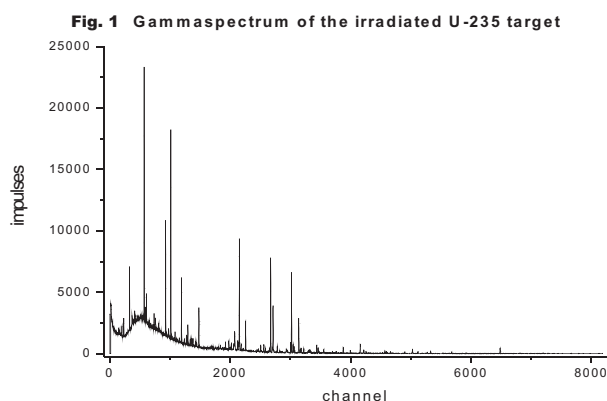
Methods

The practical part of the course started with irradiation of a set of targets, arranged in a stack (see picture above and target scheme below). After 24 hours of irradiation, the targets were left to cool for a day. After that, activity of the produced nuclides in targets was measured with alpha- and gamma detectors (fig.1). The position of the beam spot was located with autoradiography and cut out. Chemical separation of different reaction products from target material was carried out according to the procedure described in an article by Horwitz et al. [1]. Fractions produced in chemical separations were first measured with a gamma detector and then prepared as α - samples for α - spectroscopy. For each produced tracer nuclide, percentual yield in each fraction was calculated and combined as total activity (fig. 2).



Conclusions

Practical working is probably the best way to learn and understand things. In this course the degree of learning is greatly dependent on the students own activity and interest because of the intensive nature of the course; chemical separations take up to twelve hours per target and the pace of work is hectic. Despite of being challenging and demanding, this course is very satisfying and rewarding, mostly because of the inspiring visiting lecturers.



SESSION IV

Radiochemistry and Analytical Techniques

Oral presentations

Natallia Torapava

EXAFS Technique for Structure Determination of Metal Ions in Solution

Susanna Salminen, J. Suksi

Study of U Redox State During Anoxic Sample Dissolution

Rajdeep Sidhu

Radiochemistry at the Environmental Monitoring Section at Institute for Energy Technology (IFE), Kjeller, Norway

Poster presentation

Jussi Jernström, L. Perna, L. Aldave de las Heras, J. De Pablo, M. Betti, J. Lehto

Novel Chromatographic Separation Methods for Pu and Am



EXAFS technique for structure determination of metal ions in the solution

Torapava Natallia

Swedish University of Agricultural Sciences

There are a lot of processes with metal ions which take place in the aqueous medium and from this point of view it is important to know the structure of the hydrated metal ions. Structural information helps to understand and assess peculiarities of behavior of the metal ions in different natural and technological processes taking place in aqueous solutions. EXAFS (extended X-ray absorption fine structure) technique provides information about distances between atoms and coordination numbers. My research is dealing with structure determination of hydrated, solvated and hydrolyzed thorium(IV) species in both solution and solid state. I used the EXAFS method to study the structure of the hydrated thorium(IV) ion and to determine the Th-O bond distance, and from that estimate the coordination number. Th-O distance in the case of hydrated thorium appeared to be 2.45 Å which corresponds to 9-coordination, as also found in the solids $[\text{Th}(\text{H}_2\text{O})_8(\text{ClO}_4)](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ and $[\text{Th}(\text{H}_2\text{O})_6(\text{CF}_3\text{SO}_3)_3]\text{CF}_3\text{O}_3$. The Th-O bond distance in dimethylsulfoxide (dmsO) solvated thorium(IV) is ca. 2.42 Å, which corresponds to eight-coordination. The Th-O bond distance in N,N'-dimethylpropyleneurea (dmpu) solvated thorium(IV) is ca. 2.37 Å, which corresponds to seven-coordination; dmpu is a space-demanding solvent upon coordination. This shows that there is a correlation between ligand size and coordination number for thorium(IV). Hydrolysis studies of thorium(IV), it is shown that thorium(IV) concentrations below 1×10^{-5} M no precipitations take place, while centrifuging when $\text{pH} < 4$ and doesn't restrain by membrane while dialysis in pH range 1 - 4. It can be concluded that in the pH range 1 - 4 thorium(IV) is in monomeric form, and when increasing pH to above 4 thorium(IV) is restrained while centrifuging showing that thorium(IV) is in non-ionic form (probably colloids).

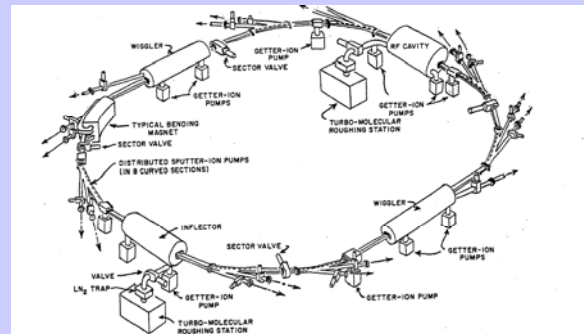
Name	Natallia Torapava
Company / University	Swedish University of Agricultural Sciences
Web-page	www.kemi.slu.se
Phone (direct line)	+46 18 671549
Fax	+46 18 673392
E-mail	Natallia.Torapava@kemi.slu.se

EXAFS technique for structure determination of metal ions in solution

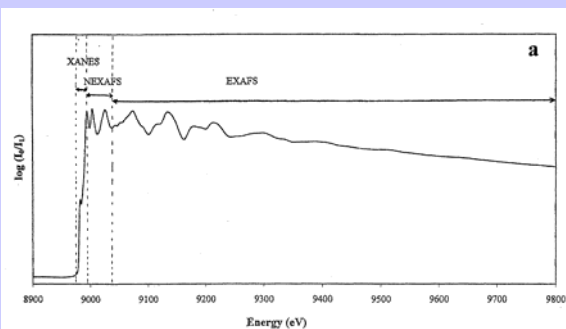
Natallia Torapava
Swedish University of Agricultural
Sciences

Uppsala, Sweden

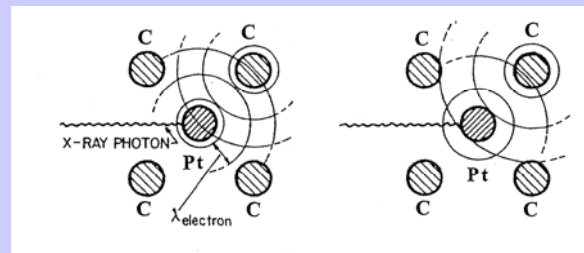
Electron-storage ring as a source of synchrotron radiation.



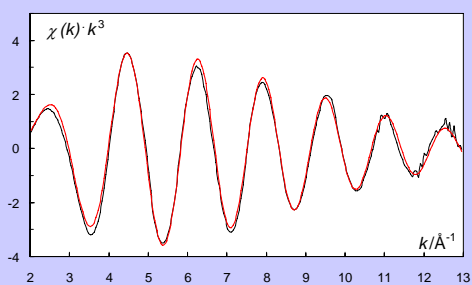
EXAFS spectrum. General view.



Schematic representation of the backscattering of platinum L_{III} edge photoelectron waves by nearest neighbor carbon atoms



EXAFS oscillations for hydrated thorium(IV) species in the liquid state.



Crystal structure of hexaaquatrisperchloratothorium(IV) perchlorate

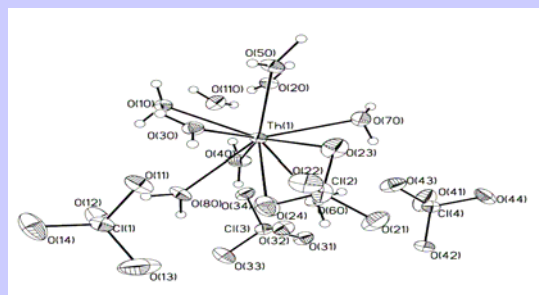
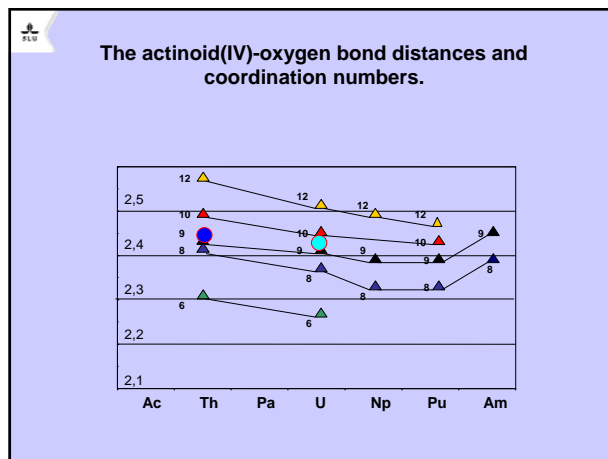


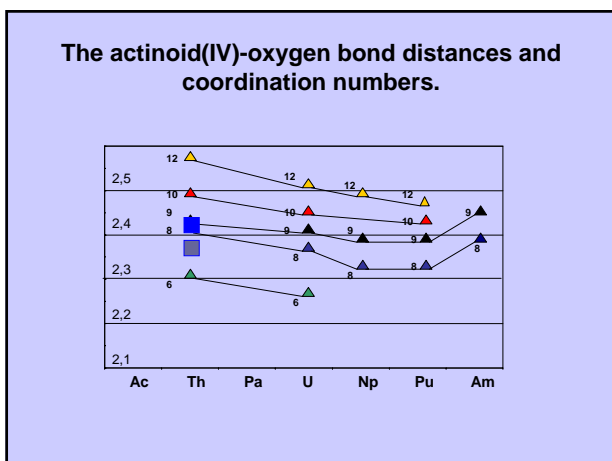
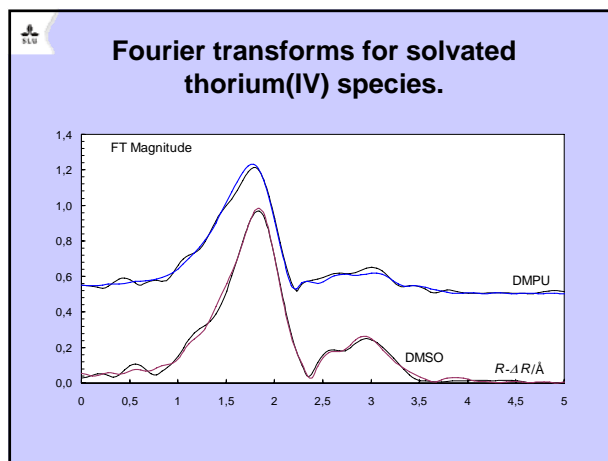
Table 1. The actinoid(IV)-oxygen bond distances depending on coordination number.

Element/CN	Th-90	U-92	Np-93	Pu-94	Am-95
6-coordinated	2.31	2.28	—	—	—
8-coordinated	2.42	2.37	2.33	2.34	2.41
9-coordinated	2.44	2.43	2.40	2.39	2.45
10-coordinated	2.50	2.45	—	2.44	—
11-coordinated	2.55	—	—	—	—
12-coordinated	2.58	2.51	2.50	2.48	—



STRUCTURE DETERMINATION OF HYDRATED THORIUM(IV) SPECIES

- The Th – O bond distance in the case of hydrated thorium(IV) appeared to be **2.45 Å** in aqueous solution, which corresponds to 9-coordination, as also found in the solids $[\text{Th}(\text{H}_2\text{O})_6(\text{ClO}_4)](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ and $[\text{Th}(\text{H}_2\text{O})_6(\text{CF}_3\text{SO}_3)_3]\text{CF}_3\text{SO}_3$.



STRUCTURE DETERMINATION OF SOLVATED THORIUM(IV) SPECIES

- The Th – O bond distance in dimethylsulfoxide solvated thorium (IV) ion is **2.42 Å** in solution, which corresponds to 8-coordination.
- The Th – O bond distance in *N,N'*-dimethylpropylene-urea solvated thorium(IV) ion is **2.37 Å** in solution, which corresponds to 7-coordination.

Hydrolysis studies for thorium(IV)

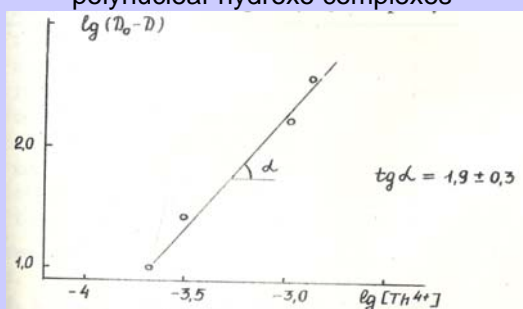
- Thorium(IV) hydrolysis at micro concentrations ($< 1 \cdot 10^{-5}$ mol/l).
- Thorium(IV) hydrolysis at high concentrations (~ 0.5 mol/l).

Interrelation of optical density and thorium(IV) concentration versus nuclearity degree

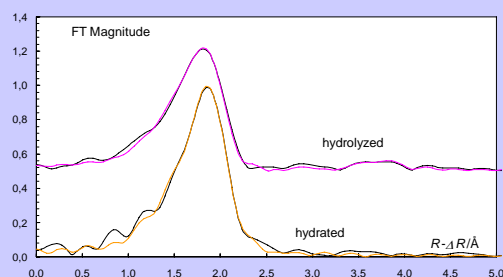
$$\lg(D_0 - D) = p \cdot \lg[Th^{4+}] + \text{const}$$

- D_0 – optical density predicted by the Lambert-Beer law
- D – optical density of thorium in the presence of polynuclear forms

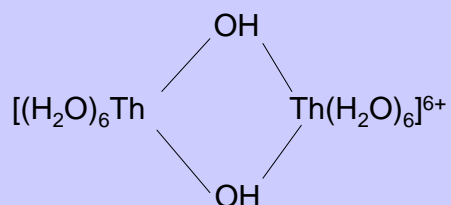
The slope ratio of $\lg(D_0 - D)$ to abscissa showing the nuclearity of thorium(IV) polynuclear hydroxo complexes



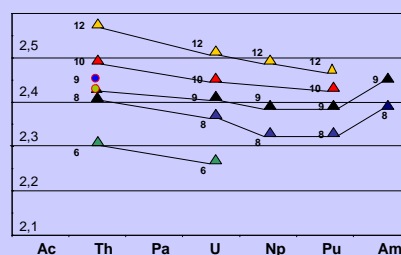
Fourier transforms of hydrated and hydrolyzed thorium(IV) species



Hydrolyzed thorium(IV) dimer structure.



The actinoid(IV)-oxygen bond distances and coordination numbers.



Conclusions.

- Hydrated thorium(IV) in aqueous solution is 9-coordinated with the mean Th – O bond distance 2.45 Å. The same coordination number has been found in the solids.
- The coordination number of dmso and dmpu solvated thorium(IV) ions is dependent on the size of solvent molecules; the more space-demanding ligand the lower coordination number and the shorter bond distance is.
- The hydrolyzed thorium(IV) complex is the dimer with double hydroxo bridge, which was confirmed both by dialysis and EXAFS studies.



Acknowledgments

- This study has been sponsored by the Visby program (Swedish Institute) and is a collaboration between the Swedish University of Agricultural Sciences and the Academy of Sciences of Belarus.
- I thank my scientific supervisor Prof. Ingmar Persson for support.



Study of changes in U oxidation states during anoxic sample dissolution


S. Salminen and J. Suksi

Laboratory of Radiochemistry, P. Box 55, 00014 University of Helsinki, Finland

Study of U oxidation states in many low U content solid samples requires wet chemical methods when instrumental techniques can not be applied. Reliable results are obtained if possible redox-perturbations during sample dissolution system are taken into account. The interferences in uranium oxidation state distribution have been investigated by adding natural iron-containing minerals to the sample dissolution system [1]. In our approach possible changes in uranium oxidation states were studied by adding U tracers $^{232}\text{U}^{4+}$ and $^{236}\text{U}^{6+}$ in sample dissolution system. The dissolution was intensified by bubbling sample solution with argon in ultrasonic bath. U oxidation states were separated from the sample solution by anion exchange and U^{4+} and U^{6+} fractions were measured by alpha spectrometry. The oxidation or reduction of U during dissolution was monitored via oxidation state change of the tracers (e. g. ^{232}U peak in U^{6+} spectrum). With this method we could eliminate all other redox-perturbations except the redox potential of a solid material itself. The dominating factor in redox balance is Fe-containing minerals which after dissolution of Fe might affect redox balance. The method was tested using varying masses of Fe-containing sample material. Sample dissolution and anion exchange operations were performed under argon atmosphere and the anoxic conditions of samples and reagents were confirmed. Experiments with $^{232}\text{U}^{4+}$ and $^{236}\text{U}^{6+}$ tracers proved that U^{4+} is unexpectedly stable against oxidation, while U^{6+} is reduced to U^{4+} significantly in the function of sample mass. Therefore, it is concluded that the reducing conditions are maintained during the dissolution and oxidation state separation procedure.

1. Ervanne, H. J. Radioanal. Nucl. Chem. Vol. 256 (3), 2003, p. 497-500

Name	Susanna Salminen
Company / University	Laboratory of radiochemistry, University of Helsinki
Web-page	http://www.helsinki.fi/kemia/radiokemia/english/
Phone (direct line)	+358 41 522 5797, +358 9 191 50137
Fax	+358 9 191 50121
E-mail	susanna.salminen@helsinki.fi




Study of U redox state during anoxic sample dissolution

Susanna Salminen and Juhani Suksi


YoungRad-seminar 14.-15.12. 2006

Faculty of natural sciences




Uranium oxidation states in geochemical environments

- Two relevant oxidation states in geochemical environments, U(IV) and (VI)
- U(IV) is sparingly soluble form of U whereas U(VI) is soluble and more mobile form of U
- Oxidation and reduction of U(IV) and U(VI) take place in sorption, dissolution, precipitation and complexation
- Environmental parameters like eH, pH, mineral composition of rock, composition of water and mineral-water interaction affect to U oxidation state
- Lower mobility of U(IV) can be utilised in nuclear waste disposal, by placing the U waste repository into bedrock composed of reducing minerals




What can U oxidation state distribution (U^{4+}/U^{total}) of solid sample tell?

- Information about environment where the sample has been taken from (oxic or anoxic conditions)
- Depth profiles of rock body, sediment or lignite formation, changes in environmental conditions during time
- Supportive information for $^{230}Th/^{234}U$ or $^{234}U/^{238}U$ activity ratio in sediment or rock sample (age dating)




U oxidation state determination from solid samples by wet chemical method

- oxidation state of U may easily change during the sample dissolution and oxidation state separation procedure
- O_2 and Fe are the most important redox-active factors disturbing the original U oxidation state distribution of sample, therefore it is essential to perform the separation procedure in anoxic conditions
- The advantages of wet chemical method, compared to instrumental techniques, are lower detection limit and easy availability (ion exchange & alpha spectrometry)
- Reliable results require elimination of interfering factors (mainly O_2) and ensuring the proper oxidation state of U tracer used in analysis



Instrumental techniques in U oxidation state determination

- EXAFS, XANES and other X-ray based spectrometries
- Non-destructive techniques
- don't have required sensitivity for environmental samples with low U concentration



The objectives of this work

- modify the existing method for U oxidation state separation for simpler and user-friendly procedure
- determine the oxidation state distribution in two different samples, U-Th ore and lignite
- investigate effect of varying solid/solution ratio in oxidation state distribution
- find out possible redox changes during sample dissolution of added U^{4+} and U^{6+} tracers



Sample 1

- Certified reference low-grade U-Th ore DL-1a (Canada)
 - U concentration 116 ppm
 - Main U minerals uraninite UO_{2+x} ($0 < x < 0.25$) and brannerite $(U,Ca,Ce)(Ti,Fe)_2O_6$
 - Oxidation state distribution previously determined in Laboratory of Radiochemistry by wet chemical method, no other results in literature (?)
 - Both U(IV) and U(VI) in sample



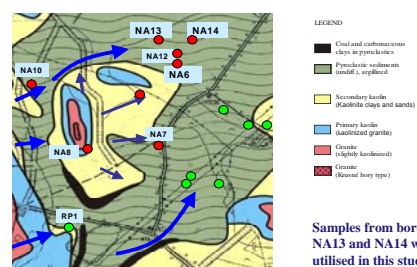
Approximate chemical composition of DL-1a.

Element	weight fraction (%)
U	0.0116
Fe	0.9
S	0.4
Al	5.3
Ca	0.29
K	0.23
Mg	0.19
Si	40

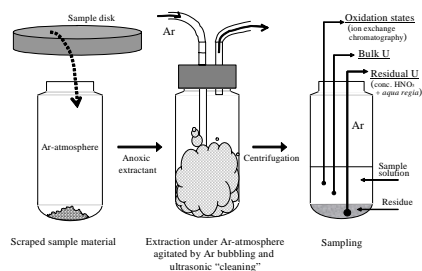


Sample 2

- Lignite samples from so-called clay/lignite sand horizon of Ruprechtov natural analogue site (Germany)
 - Depth of sampling was 54-60 m
 - U is accumulated in layers
 - Varying sample composition
 - Uranium concentration ~300 ppm



Experimental procedure



Experimental procedure, contd.

- Extraction time was 10 minutes
- aliquots for total U determination (to check the complete dissolution of U) and oxidation state determination
- Oxidation states were separated by ion exchange in Ar atmosphere
- Second ion exchange for U(IV) and U(VI) fractions (purification from Th, Ra and its daughters)
- Micro-coprecipitation of U with CeF_3
- Activity determination of U(IV) and U(VI) by alpha spectrometry



Preparing $^{232}\text{U}^{4+}$ tracer and ensuring the right oxidation state

- Known amount of ^{232}U tracer solution was reduced with $\text{TiCl}_3 \rightarrow ^{232}\text{U}^{4+}$ in argon-bubbled extraction solution (4 M HCl + 0.03 M HF)
- Re-oxidation of U^{4+} was monitored and after 3 days small fraction of U (2% of total) was oxidised to U^{6+}
- To ensure that all U in tracer was in U^{4+} form, after 3 days from preparing tracer, U^{4+} and U^{6+} were separated from each other and U^{4+} fraction was immediately used for sample extraction



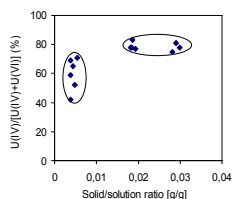
Experiment with both U^{4+} and U^{6+} tracers

- Both $^{232}\text{U}^{4+}$ and $^{236}\text{U}^{6+}$ were added to sample dissolution system before extraction
- Three solid/solution ratios were tested (DL-1a)
- From alpha spectra of separated U(IV) and U(VI) fractions could be seen if tracer(s) had been oxidised or reduced during the analysis procedure



Results: U oxidation state distribution as a function of DL-1a sample mass

Sample mass (mg)	U(IV)/[U(IV)+U(VI)] (%)
40	0,42
40	0,59
41	0,69
47	0,65
52	0,52
58	0,71
192	0,78
196	0,78
197	0,83
205	0,77
298	0,75
308	0,81



Results: U oxidation state distribution in lignite samples

- Samples 13NA and 14NA were assumed to have similar U oxidation state distributions due to similar sampling site and composition
- We used large masses in extraction because previously performed double-tracer tests with DL-1a proved the necessity of new experiment with high solid-solution ratio (will be explained later)
- 13NA proved to be unsuitable sample for this study having low fraction of reduced uranium
- U did not dissolve quantitatively from lignite samples (80% dissolved)



Results for lignite samples, contd.

Sample	Mass (g)	U(IV)/[U(IV)+U(VI)] (%)
13NA	1513	7
"	854	20
"	1237	8
14NA	993	30
"	922	27
"	901	32



Results $^{232}\text{U}^{4+}$ oxidation during sample dissolution

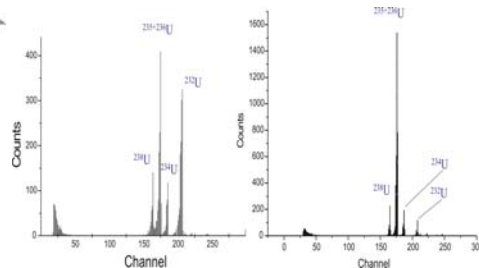
Sample	description	mass (mg)	Oxidised ^{232}U -total ^{232}U (%)
1a	lignite	50	0,27
1b	"	123	0,29
2a	"	207	0,39
2b	"	442	0,24
3a	"	200	0,50
3b	"	248	0,73
1	DL-1a	49	1,4
2	"	175	0,8
3	"	293	0,5



Results from double tracer test (DL-1a ore)

- Tracer $^{232}\text{U}^{4+}$ was stable against oxidation during extraction and separation procedure, only <2% of added was present in U^{6+} fraction
- On the other hand, tracer $^{236}\text{U}^{6+}$ was reduced during the analysis procedure, quantitatively with the highest solid/solution ratio

DL-1a	Mass (mg)	U(IV) in U(VI) (%)	U(VI) in U(IV) (%)
1	48	2.6	16
2	120	1.1	48
3	499	0.1	100



Alpha spectra of Sample 2 from experiment where both $^{232}\text{U}^{4+}$ and $^{236}\text{U}^{6+}$ were added before the extraction. Left: Spectrum of the U(IV) fraction, the counting time was 619 minutes. Note the large ^{236}U tracer peak indicating the reduction of $^{236}\text{U}^{6+}$. Right: Spectrum of the U(VI) fraction, the counting time was 2760 minutes.



Conclusions

- Oxidation of U^{4+} due to atmospheric oxygen during extraction and $\text{U}^{4+}/\text{U}^{6+}$ separation could be avoided
- Increasing solid/solution ratio \rightarrow increasing amount of
 - reduced natural U
 - reduced U^{6+} tracer
- more dramatic effect on tracer U than natural U, difference in redox reaction kinetics?
- POSSIBLE REASON: increasing amount of Fe^{2+} -minerals capable for reducing U(VI)?
- More sample analyses with high solid/solution ratio are needed



Conclusions

In the beginning we considered external interference, O_2 , as the most likely factor for changing U oxidation state distribution of samples and tracers by oxidising U in sample-solution system. Instead, we made opposite observations about reduction of U, which may be due to internal redox interferences (dissolution of Fe^{2+} -rich sample matrix) and cannot be fully explained yet.



Future work

- Evaluation of uncertainties in results
- Comparison of wet chemical method with EXAFS and XANES: U oxidation state distribution in DL-1a and lignite samples
- Measurements in Karlsruhe (ANKA) in March 2007, if funding is admitted



Radiochemistry at the Environmental Monitoring Section at Institute for Energy Technology (IFE), Kjeller, Norway

Rajdeep Sidhu

Environmental Monitoring Section, Health and Safety Department,
Institute for Energy Technology, Kjeller, Norway

The Environmental Monitoring Section monitors radioactive pollutions and studies the mechanisms influencing the dispersion and transfer of radioactive materials in nature. The section is responsible for control of radioactive discharges from IFE's nuclear activities at Kjeller and for monitoring of radioactive contamination in the local environment. The Environmental Monitoring Section runs one of Norway's leading laboratories for analyses of radioactivity in environmental samples.

The section performs analysis of anthropogenic and natural radionuclides in a variety of sample materials in connection with discharge control, environmental monitoring, research projects, and on assignment from external customers. In many cases a chemical separation of the element of concern must be performed before activity measurement. The measurements may often be performed directly on the sample, or following a simple pre-treatment. When measuring pure alpha or beta emitters or nuclides with very weak gamma lines, the nuclide of concern must be separated chemically before measuring by alpha spectrometry or gross beta counting respectively.

Some of the radiochemical procedures in use, and procedures in development will be presented.

Name	Rajdeep Sidhu
Company / University	Institute for Energy Technology, IFE
Web-page	www.ife.no
Phone (direct line)	+47 63 80 60 53
Fax	+47 63 81 25 61
E-mail	rajdeep.sidhu@ife.no

Radiochemistry at the Environmental Monitoring Section at Institute for Energy Technology (IFE), Kjeller, Norway

Rajdeep Sidhu

15.01.2007



Environmental Monitoring Section

- 9 employees
- Environmental monitoring programme
 - Low-level liquid radioactive effluents
 - Environmental samples from the surroundings
- Personnel monitoring (bioassay)
- Research projects
- Commercial services

15.01.2007



Low-level liquid radioactive effluents

- Collected in large tanks for characterization prior to discharge
- Discharged after determination of gamma-emitters
- Analysed radiochemically for ^{90}Sr , U-, Pu-, Am- and Cm-isotopes

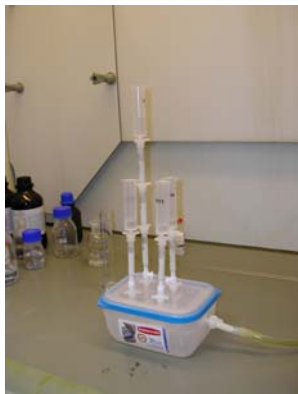
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^{90}Sr , U-, Pu-, Am- and Cm-isotopes in liquid effluents

- 200 ml sample added tracers is evaporated and dry ashed
- Dissolved in 3 M HNO_3 added sulfamic acid, ascorbic acid and $\text{Al}(\text{NO}_3)_3$ (Fe(II), Pu(III))
- Loaded on UTEVA-TRU-Sr columns coupled together
- On-column oxidation of Pu(III) to Pu(IV) with NaNO_2
- UTEVA: U(VI) eluted with 0.01 M HCl
- TRU: Am(III) and Cm(III) eluted with 4 M HCl
Pu(III) eluted with 4 M HCl and TiCl_3
- Sr: Sr eluted with 0.05 M HNO_3 (ingrowth of ^{90}Y)

15.01.2007



15.01.2007



Environmental Monitoring Programme



15.01.2007



Samples

- NALFA
 - Sediment (γ -emitters and Pu)
 - Water (γ -emitters, ^3H and ^{90}Sr)
- Rain water (γ -emitters, ^3H , ^{90}Sr and Pu)
- Farms
 - Milk (γ -emitters and ^{90}Sr)
 - Agricultural products (γ -emitters, ^{90}Sr and Pu)
- Gras (γ -emitters, ^{90}Sr and Pu)
- River
 - Water (γ -emitters, ^3H , ^{90}Sr and Pu)
 - Sediment (γ -emitters, ^{90}Sr , U and Pu)
 - Fish (γ -emitters, ^{90}Sr and Pu)
 - Water plants (γ -emitters, ^{90}Sr and Pu)

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Ion exchange separation of Pu

- Preconcentration (drying, ashing, precipitation, evaporation)
- Leaching of Pu with conc. acids
- Large samples
 - Evaporation and dissolution in 8 M HCl
 - 10% TIOA/xylene extraction
- Smaller samples
 - Evaporation and dissolution in 8 M HNO_3
 - Separation on AG1-X4
- Source preparation: electrodeposition

15.01.2007



Ex.chrom separation of Sr and Pu (sediment)

- Drying and ashing
- Leaching with aqua regia
- Evaporation and dissolution in dilute HCl
- Oxalate precipitation followed by ashing
- Dissolution in 3 M HNO_3 added sulfamic acid, ascorbic acid and $\text{Al}(\text{NO}_3)_3$ (Fe(II), Pu(III))
- Loaded on TRU-Sr columns coupled together
- TRU: Pu(III/IV) (source prep.: co-precipitation)
- Sr: Sr

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Sr, U, Pu and Am in urine

- Phosphate precipitation followed by ashing
- Dissolution in 3 M HNO_3 added sulfamic acid, ascorbic acid and $\text{Al}(\text{NO}_3)_3$ (Fe(II), Pu(III))
- Load on UTEVA-TRU-Sr columns coupled together
- UTEVA: U(VI)
- TRU: Pu(III/IV), Am(III), Cm(III)
- Sr: Sr

15.01.2007



Commercial services

- ^{210}Pb , ^{226}Ra and ^{228}Ra in produced water
- U and Th in materials from Si production
- Sr, U and Th in artificial fertilizer
- Sr in seawater
- ...

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^{210}Pb , ^{226}Ra and ^{228}Ra in produced water

- 2 litre produced water is heated with HNO_3 and MnO_4^- after addition of ^{133}Ba tracer
- pH adjustment to 1-2
- Reduction of MnO_4^- to MnO_2
- Addition of sulphate (H_2SO_4 and Na_2SO_4)
- Addition of Pb and Ba ($\text{Pb}(\text{Ba})\text{SO}_4$)
- Collection of MnO_2 and $\text{Pb}(\text{Ba})\text{SO}_4$
- Drying of the precipitate
- Gamma determination of ^{210}Pb , ^{226}Ra and ^{228}Ra

15.01.2007



U and Th in materials from Si production

- Dissolution of Si-materials with HNO_3 – HF
- $\text{Fe}(\text{OH})_3$ precipitation of U and Th
- Dissolution and evaporation
- Dissolution in 3 M HNO_3 added sulfamic acid, ascorbic acid and $\text{Al}(\text{NO}_3)_3$ (Fe(II))
- Load on UTEVA
- UTEVA: Th(IV) eluted with 4 M HCl
U(VI) eluted with 0.01 M HCl
- Source prep.: co-precipitation

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Sr, U and Th in artificial fertilizer

- Partial dissolution with HNO_3 – oops Sr is fixed to the undissolved material
- Ashing and partial dissolution with HNO_3 – oops Sr is fixed to the undissolved material
- Partial dissolution with HNO_3
- Ashing of the undissolved material
- Fusion with $\text{Li}_2\text{B}_4\text{O}_7$
- Dissolution with 3 M HNO_3
- Separation using UTEVA coupled on Sr-Resin

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^{90}Sr in seawater

- ^{90}Sr co-precipitation with $\text{Ca}(\text{Sr})\text{CO}_3$
- Sr separation from Ca by repeated nitrate precipitations
- Sr separation from Y by repeated hydroxide precipitations
- Sr separation from Ba, Ra and Pb by repeated chromate precipitations
- Ingrowth of ^{90}Y
- ^{90}Y separation from ^{90}Sr by hydroxide and sulphate precipitations

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^{90}Sr in seawater – method under development

- Acidification and equilibrium between ^{90}Sr and ^{90}Y
- Co-precipitation of ^{90}Y with $\text{Fe}(\text{OH})_3$
- Dissolution and evaporation
- Y extraction with TBP from 14 M HNO_3
- Y strip with H_2O
- Is further separation from Th required? Phosphate precipitation of Th?
- Further Y separation and source preparation by hydroxide and oxalate precipitation

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Radioactivity in Produced Water from Norwegian Oil and Gas Installations

- Determination of ^{226}Ra and ^{228}Ra in:
 - Fish and bottom feeders
 - Seawater

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^{226}Ra and ^{228}Ra in fish and bottom feeders

- Drying and ashing
- Dissolution with HNO_3
- Large amount of Ca in bone will cause problems for Ra (nitrate precipitation?)
- PbSO_4 co-precipitation of Ra
- Dissolution with DTPA
- BaSO_4 co-precipitation of Ra → α -spec.
- Ingrowth of ^{228}Th from ^{228}Ra → Th separation and α -spec

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^{226}Ra and ^{228}Ra in seawater

- MnO_2 co-precipitation of Ra (pH 7-8!!)
- Washing of the precipitate (wash out traces of Ca)
- Dissolution with $\text{HCl} - \text{H}_2\text{O}_2$
- PbSO_4 co-precipitation of Ra
- Dissolution with DTPA
- BaSO_4 co-precipitation of Ra $\rightarrow \alpha$ -spec.
- Ingrowth of ^{228}Th from $^{228}\text{Ra} \rightarrow \text{Th}$ separation and α -spec

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Puffing on Polonium

The New York Times

A fraction of a trillionth of a curie may not sound like much, but remember that we're talking about a powerful radionuclide disgorging alpha particles — the most dangerous kind when it comes to lung cancer — at a much higher rate even than the plutonium used in the bomb dropped on Nagasaki. Polonium 210 has a half life of about 138 days, making it thousands of times more radioactive than the nuclear fuels used in early atomic bombs

By ROBERT N. PROCTOR Published: December 1, 2006

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Novel chromatographic separation methods for Pu and Am

Jernström, J.^a, Perna, L.^b, Aldave de las Heras, L.^c,
De Pablo, J.^d, Betti, M.^c, Lehto, J.^a

a Laboratory of Radiochemistry, University of Helsinki

b Institute for the Protection and Security of the Citizen IPSC, European Commission

c Institute for Transuranium Elements ITU, European Commission

d Chemical Engineering Department, Universidad Politecnica de Catalunya

An on-line method has been developed for separating americium from environmental samples. The procedure utilizes extraction chromatography (TEVA, Eichrom) to separate americium from light lanthanides, and cation exchange (TCC-II, Dionex) to concentrate americium before the final separation in an mixed-bed ion chromatography column (CS5A, Dionex). The separated radiochemically pure americium fraction is measured by alpha spectrometry. The method has been tested with certified sediment and soil samples and found to be applicable for the analysis of environmental samples containing a wide range of Am-241 activity.

Proceeding from the on-line method developed for americium, a method has also been developed for separating plutonium and americium. Plutonium is reduced to Pu(III), and separated together with Am(III) throughout the procedure. In the final stage of the process, Pu(III) and Am(III) are eluted from the ion chromatography column as anionic dipicolinate and oxalate complexes, respectively, and measured by alpha spectrometry.

Name	Jussi Jernström
Company / University	University of Helsinki
Web-page	http://www.helsinki.fi/kemia/radiokemia/english/
Phone (direct line)	+358 9 191 50131
Fax	+358 9 191 50121
E-mail	jussi.jernstrom@helsinki.fi

Novel chromatographic separation methods for Pu and Am

^a Jernström, J., ^b Perna, L., ^c Aldave de las Heras, L., ^d De Pablo, J., ^c Betti, M., ^a Lehto, J.

^a Laboratory of Radiochemistry, University of Helsinki

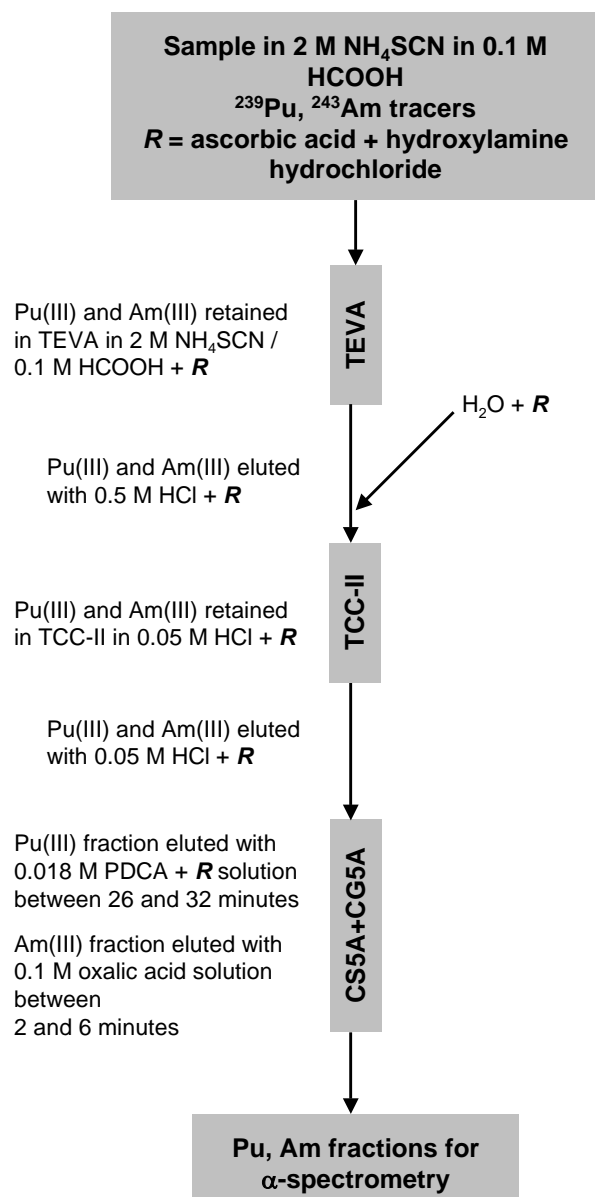
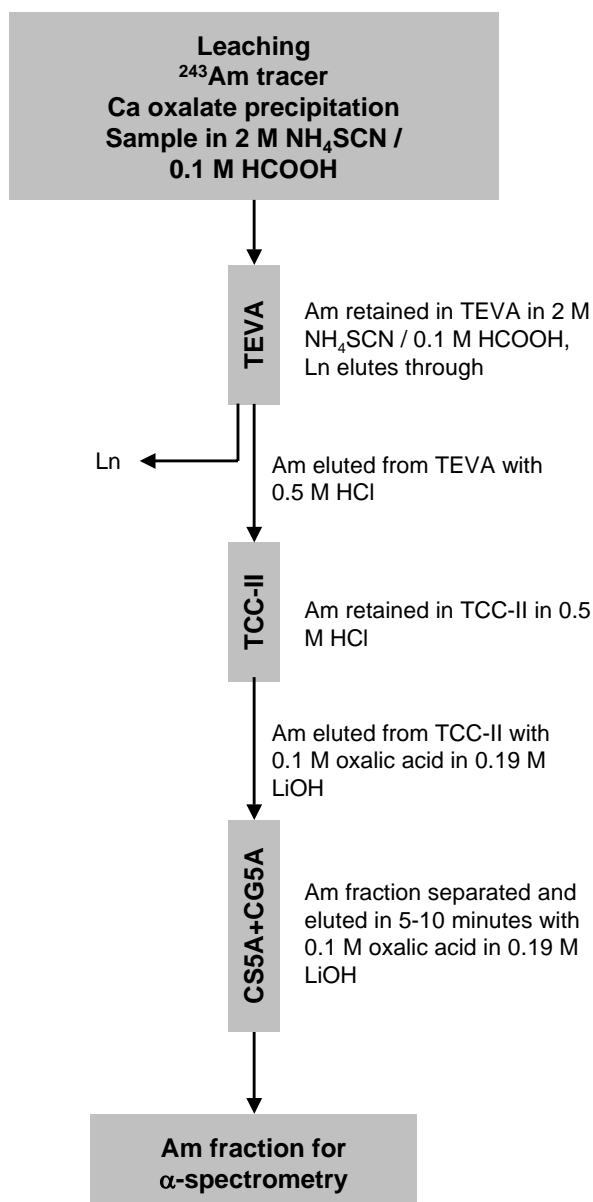
^b Institute for the Protection and Security of the Citizen IPSC, European Commission

^c Institute for Transuranium Elements ITU, European Commission

^d Chemical Engineering Department, Universidad Politecnica de Catalunya

- Two on-line methods were developed:
 - separation of Am from sediment and soil samples
 - separation of Pu and Am from tracer solutions
- Use of ion exchange and chromatography:
 - extraction chromatography (TEVA, Eichrom)
 - cation exchange (TCC-II, Dionex)
 - ion chromatography (CS5A, Dionex)

- Benefits:
 - reduced analysis time
 - reduced sample handling (contamination risk)
 - automatization possible





Contact information, non-presenting participants

Name	Jon Drefvelin
Company / University	Norwegian Radiation Protection Authority (NRPA)
Web-page	www.nrpa.no
Phone (direct line)	+47 67 16 26 16
Fax	+47 67 14 74 07
E-mail	jon.drefvelin@nrpa.no

Name	Kai Hämäläinen
Company / University	Dating laboratory / University of Helsinki
Web-page	www.fmn.helsinki.fi/english/datinglab/
Phone (direct line)	+358 9 19150743
Fax	+358 9 191 50741
E-mail	Kai.Hamalainen@Helsinki.Fi

Name	Kerttuli Helariutta
Company / University	University of Helsinki
Web-page	www.helsinki.fi/kemia/radiokemia
Phone (direct line)	+358 9 19150133
Fax	+358 9 19150121
E-mail	kerttuli.helariutta@helsinki.fi

Name	Nina Huittinen
Company / University	University of Helsinki
Web-page	www.helsinki.fi/kemia/radiokemia
Phone (direct line)	+358 44 2950969
Fax	+358 9 19150121
E-mail	nina.huittinen@helsinki.fi

Name	Stefan Isaksson
Company / University	Gammadata Instrument AB
Web-page	www.gammadata.se
Phone (direct line)	+46 18 480 58 07
Fax	+46 18 55 58 88
E-mail	Stefan.Isaksson@gammadata.se



Name	Jarno Jalomäki
Company / University	University of Helsinki
Web-page	www.helsinki.fi/kemia/radiokemia
Phone (direct line)	+3589407084488
Fax	+358 9 19150121
E-mail	jarno.jalomaki@helsinki.fi

Name	Göran Jonsson
Company / University	Gammadata Instrument AB
Web-page	www.gammadata.se
Phone (direct line)	+46 18 480 58 20
Fax	+46 18 55 58 88
E-mail	Goran.Jonsson@gammadata.se

Name	Teija Koivula
Company / University	Laboratory of Radiochemistry, University of Helsinki
Web-page	www.helsinki.fi/kemia/radiokemia
Phone (direct line)	+358 9 191 50 134
Fax	+358 9 191 50 121
E-mail	teija.s.koivula@helsinki.fi

Name	Jyri Lehto
Company / University	MAP Medical Technologies Oy
Web-page	www.mapmedical.fi
E-mail	jyri.lehto@helsinki.fi

Name	Astrid Liland
Company / University	Norwegian Radiation Protection Authority (NRPA)
Web-page	www.nrpa.no
Phone (direct line)	+47 67 16 25 38
Fax	+47 67 14 74 07
E-mail	astrid.liland@nrpa.no



Name	Mervi Söderlund
Company / University	University of helsinki
Web-page	www.helsinki.fi/kemia/radiokemia
Phone (direct line)	+47 44 5451943
Fax	+358 9 191 50 121
E-mail	mervi.soderlund@helsinki.fi

Name	Hanna Tuovinen
Company / University	MAP Medical Technologies Oy
Web-page	www.mapmedical.fi
E-mail	hanna.p.tuovinen@helsinki.fi

Concluding remarks

Some questions were raised after the seminar to initiate a plenary discussion among the participants.

- Do you think this seminar was a good idea?
- Do you consider the seminar successful?
- Should a seminar like this be repeated on a regular basis? If yes, how often?
- How can we get more participants to a seminar like this?

Most importantly, the participants agreed that the seminar was a good idea and that it had been successful.

Comments from the participants:

- Some students had never heard about the NKS before the YoungRad seminar. It was therefore suggested that the NKS should market themselves towards more institutions than today.
- The low number of participating students can be partly explained by the fact that this was the first seminar of its kind in the Nordic countries. Once the rumours about the successful seminar start to spread, more students will want to participate in future seminars.
- Some students could not participate in the seminar because they had exams during the same period.
- It was difficult recruiting students from Denmark. Not because the students did not want to participate, but because their supervisors did not want them to participate. It can be explained by several factors, e.g limited traveling budget combined with other relevant international conferences coming up next year. If more YoungRad seminars are to be arranged, special attention should be paid on informing professors and supervisors of students in all Nordic countries. Positive attitude of these senior scientists towards the seminar can encourage their students to participate.
- PhD students have limited conference travel funding, and will therefore often choose a more relevant conference than YoungRad. On the other hand, NKS could sponsor the travel expenses of students to facilitate their participation.
- The main target group for the seminar should be PhD students. However, the mixture of participants with most PhD students, some undergraduate students, authorities, research and industry personnel at this seminar was good, and the aim must be to keep this variety in future seminars.
- It is important for students to meet other young people that work with similar subjects.
- It is nice for students to experience that there is a life outside the laboratory and the university.
- The low recruitment of students to these fields has been widely discussed earlier, but little has been done. Now the NKS has done something and should brag about it!

Comments from the Norwegian Radiation Protection Authority:

- The NRPA experiences difficulties in finding people with relevant background to important positions at the NRPA. A seminar like YoungRad is important for securing future recruitment of personnel
- All subjects covered by the seminar are relevant for the NRPA, and this broadness in subjects should be kept in future seminars.
- The YoungRad seminar should be arranged on a regular basis, but the location of the seminar should alternate between the Nordic countries.

Some questions were also raised to the NKS:

- Do the NKS feel that it is worth the money to sponsor a seminar like the YoungRad seminar?
- Has the expectations for the seminar been reached?
- Will the NKS be interested in making such a seminar a tradition?

Comments from the NKS:

- It is important that the young generation themselves arrange seminars like this. This will give them a better feeling of ownership to the seminar.
- Could it be suggested to arrange a YoungRad seminar every second year, with a NKS summary seminar the years between?
- The young generation can take responsibility and “advertise” for the NKS to get more institutions involved in the Nordic co-operation.



List of participants, YoungRad-seminar Helsinki, 14-15 December 2006

No.	Name	Institution, country
1	Drefvelin, Jon	Norwegian Radiation Protection Authority
2	Fure, Kristin	Institute for Energy Technology, Norway
3	Gustafsson, Håkan	Linköping University, Sweden
4	Hartvig, Sven K.	Institute for Energy Technology, Norway
5	Helariutta, Kerttuli	University of Helsinki, Finland
6	Helin, Semi	Turku PET Centre, University of Turku, Finland
7	Holm, Joachim	Chalmers University of Technology, Sweden
8	Huittinen, Nina	University of Helsinki, Finland
9	Hämäläinen, Kai	University of Helsinki, Finland
10	Isaksson, Stefan	Gammadata, Sweden
11	Jalomäki, Jarno	University of Helsinki, Finland
12	Jernström, Jussi	University of Helsinki, Finland
13	Jokelainen, Lalli	University of Helsinki, Finland
14	Jonsson, Göran	Gammadata, Sweden
15	Kelokaski, Maarit	University of Turku, Finland
16	Kirjavainen, Anna	University of Turku, Finland
17	Knutsson, Andreas	Chalmers University of Technology, Sweden
18	Koivula, Risto	University of Helsinki, Finland
19	Koivula, Teija	University of Helsinki, Finland
20	Kyllönen, Jarkko	University of Helsinki, Finland
21	Kärkelä, Teemu	VTT, Finland
22	Lehto, Jyri	MAP Medical Technologies Oy, Finland
23	Leskinen, Anumaija	University of Helsinki, Finland



No.	Name	Institution, country
24	Liland, Astrid	Norwegian Radiation Protection Authority
25	Lind, Ole-Christian	Norwegian University of Life Sciences
26	Lipponen, Tiina	University of Helsinki, Finland
27	Magnusson, Åsa	Lund University, Sweden
28	Makkonen-Craig, Stewart	University of Helsinki, Finland
29	Mononen, Heli	STUK, Finland
30	Paintner, Risto	MAP Medical Technologies Oy, Finland
31	Palosaari, Miia H.	University of Helsinki, Finland
32	Petersen, Roongrat	DTU, Denmark
33	Rokka, Johanna	Turku PET Centre, University of Turku, Finland
34	Salminen, Susanna	University of Helsinki, Finland
35	Sidhu, Rajdeep	Institute for Energy Technology, Norway
36	Strålberg, Elisabeth	Institute for Energy Technology, Norway
37	Söderlund, Mervi	University of Helsinki, Finland
38	Togneri, Laura	University of Helsinki, Finland
39	Torapava, Natallia	Swedish University of Agricultural Sciences
40	Tuovinen, Hanna	MAP Medical Technologies Oy, Finland
41	Vaaramaa, Kaisa	University of Helsinki, Finland
42	Ylipieti, Jarkko	STUK (Rovaniemi), Finland
43	Zakaria, Mohamad	Malmö Högskola, Sweden



YoungRad participants in the auditorium at Hotel Arthur. Not all participants were present when the picture was taken (photo: Sigurður Emil Pálsson)

Title	YoungRad-seminar. Proceedings. Seminar for young scientists in the fields of radiophysics, radiochemistry, radioecology, radiation protection and related fields. Helsinki 14-15 December 2006
Author(s)	Elisabeth Strålberg (ed.) ¹ , Roongrat Petersen ² , Susanna Salminen ³ and Rajdeep Sidhu ¹
Affiliation(s)	¹ Institute for Energy Technology, Norway ² Technological University of Denmark, Denmark ³ University of Helsinki, Finland
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No. of illustrations	-
No. of references	-
Abstract	<p>To provide an inspiring working environment for young students and scientists, it is important that they at an early stage can take part in a network of scientists working in their fields of interest. However, within each of the five Nordic countries the network of people involved in the fields of radiophysics, radiochemistry, radioecology, radiation protection and other related fields is rather small. Educational networking is a key factor in keeping young researchers motivated to continue working within these fields, and to recruit new students.</p> <p>For that reason the first YoungRad-seminar was held in Helsinki 14-15 December 2006. 43 young participants including MSc and PhD students at universities, researchers at different institutes and personnel from Nordic authorities took part in the seminar. All Nordic countries except Iceland were represented. The seminar was divided into four sessions including oral and poster presentations. In addition two senior researchers were invited to speak about Nordic radioecology and NKS. This report contains the abstracts and presentations made at the seminar.</p>
Key words	Seminar, young scientists, radiophysics, radiochemistry, radioecology, radiation protection